SYNTHESIS OF CLAY MINERALS

A THESIS

Presented to

The Faculty of the Graduate Division

by

Numan Abdul-Latif

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemical Engineering

Georgia Institute of Technology

April, 1969

SYNTHESIS OF CLAY MINERALS

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ACKNOWLEDGMENTS

The author gratefully acknowledges his thesis advisor, Dr. Charles E. Weaver, for suggesting the problem and for his continuous help and advice during this investigation. Professor Kevin C. Beck is deeply appreciated for his helpful suggestions and for serving on the reading committee. Appreciation is also extended to Dr. Clyde Orr, Jr. for his conscientious service as a member of the reading committee.

It is a pleasure to acknowledge assistance from the National Science Foundation (Grant GA-1330) to whom the author is deeply indebted.

Dr. Grover L. Bridger, Director of the School of Chemical Engineering, is greatly appreciated for lending the author the pressure reaction apparatus used in part of this work. Thanks to Mr. T. D. Oulton of Engelhard Minerals and Chemicals Corporation, New Jersey, for providing an ample specimen of attapulgite. The International Nickel Company is acknowledged for donating the nickel pipe and bar used for the manufacture of the pressure bombs. The author wishes to thank the DuPont de Nemours and Company for donating samples of sodium metasilicate and Ludox SM. Dr. Gerardo E. Bossi has been very helpful to the author, especially in the field of x-ray diffraction. Shop machinists, Mr. Thomas Mackrovitch and Mr. C. E. Mayes, made the pressure bombs and their work is acknowledged.

Finally, thanks are given to Mrs. Dianne Clark who typed part of this work for two publications.

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SUMMARY

Studies concerning the synthesis of clay minerals have been conducted at room temperature as well as at hydrothermal conditions. However, there are a number of discrepancies in the results of the different investigators, especially for the systems $MgO-SiO_2-H_2O$ and $MgO-Al_2O_3-SiO_2-H_2O$.

The present investigation is restricted mainly to the systems $MgO-SiO_2-H_2O$ and $MgO-Al_2O_3-SiO_2-H_2O$ under alkaline conditions and over the temperature range of 25° to 200°C. The methods tried were the reaction in solution of the system $Mg-Al-SiO_2$ and the reaction of Mg-Al double hydroxides with aqueous silica solution. Reaction products were checked by x-ray diffraction, chemical analysis, and some by electron microscopy. In the system $Mg-SiO_2-H_2O$ and over the temperature range of 25° to 200°C, the lower temperatures favor the formation of 2:1 layer silicates, while the higher temperatures favor the formation of 1:1 layer silicates. Aqueous silica reaction with Mg-Al double hydroxides containing low Mg/Al ratio leads to the formation of montmorillonite; whereas, with double hydroxides containing high Mg/Al ratio, saponite is formed. Serpentine minerals are formed in the intermediate composition of double hydroxides. Pure $Al(OH)_3$ forms boehmite while pure $Mg(OH)_2$ forms serpentine minerals. These serpentine minerals were found to have slightly different spacings, depending on the Mg/Al ratio of the reactant. The larger this ratio the larger the spacing.

Particular interest is focused on the chain structure clay minerals, attapulgite, and sepiolite. Although the molecular structures of attapulgite and sepiolite have been carefully studied by Bradley,[6] Nagy and Bradley,[7] and Brauner and Preisinger,[8] these are, among the clay minerals, the least understood.

The field of stability of attapulgite and sepiolite in water and in $MgCl_2$ and $AlCl_3$ solutions was studied in order to determine the temperature range at which these two minerals, in equilibrium with the above solutions, may exist. Attapulgite decomposes at about 175° C under equilibrium water pressure in solution containing aluminum ions under alkaline conditions. Sepiolite decomposes at about 140° C. Therefore, under these conditions attapulgite has a wider field of stability than sepiolite.

The activity product constants for attapulgite and sepiolite were calculated from their solubility data in water at room temperature. Using the Nernst equation, their standard free energies of formation were determined. The purpose of determining the activity product constant and the standard free energy of formation was to locate the concentration boundaries, including the hydrogen ion concentration, at which these minerals may exist when in equilibrium with solution. In addition, relative stability compared to the other minerals may be obtained from the above calculation. The standard free energy of formation for dehydrated sepiolite, $Mg_2Si_3O_8$, was found to be -908.8 ± 0.5 kcal/mole. For attapulgite, ΔF_f° was found to be -2828.7 kcal/mole of $Mg_{2.86}Al_{1.43}Si_8O_{20}(OH)_2 8H_2O$.

Attapulgite and sepiolite were digested with large excess of

hydrochloric acid at constant temperatures for various periods of time. The reaction was found to be of first order with respect to Mg, Al, and Fe components in the clay and also with respect to the acid concentration.

Osthaus[42,43] found that montmorillonite and nontronite had equal reaction rate constants for Mg, Al, and Fe. For attapulgite, the reaction rate constant was found to be the largest for Mg and smallest for Al, with Fe having an intermediate reaction rate constant. One explanation is that Al is concentrated in the interior position of the octahedral structure, while Mg and Fe are concentrated in the edge positions; whereas, in montmorillonite the distribution is random.

The reaction rate constant of Mg in sepiolite is about 240 times that for attapulgite. This may be an indication that sepiolite is less stable to chemical weathering than attapulgite.

The activation energies for Mg, Al, and Fe in attapulgite were found to be essentially identical and equal to about 18.4 kcal/mole. This is similar to the value found by Osthaus[43] for montmorillonite.

Treatment of partially acid-digested attapulgite with magnesium ions under alkaline conditions resulted in an increase in the x-ray intensity of the 10.5 Å spacing, suggesting that some of the attapulgite was reconstituted.

Some of the hypotheses of the origin of attapulgite and sepiolite were reviewed. However, under the experimental conditions employed, none of them proved to be satisfactory.

CHAPTER I

INTRODUCTION

A large number of investigations have been conducted on the synthesis of clay minerals at room temperatures as well as at hydrothermal conditions. However, there is considerable discrepancy and confusion in the results of the different investigators, especially for the systems $MgO\text{-}SiO_2 H_2O$ and $MgO\text{-}Al_2O_3\text{-}H_2O$.

To illustrate, Yang[1] studied the reactions in the ternary system $MgO\text{-}SiO_2\text{-}H_2O$ over the temperature range 100° to 300°C and found only two phases were produced. Under conditions between 100° to 200°C and atmospheric pressure to 20,000 psi, the predominant magnesium silicate was found to be serpentines regardless of the initial MgO/SiO_2 ratio. In the range 200° to 300°C and between 210 and 20,000 psi, two stable phases, serpentine and talc, were observed. The proportion of serpentine and talc in the product depended on the initial composition of the reaction mixture. Siffert[2] and Siffert and Wey[3] reported that in an alkaline medium at ordinary temperature, magnesium reacts with monomolecular silica solution to form sepiolite. However, Preisinger[4] mentioned that sepiolite could not be formed in the system $MgO\text{-}SiO_2\text{-}H_2O$ within the temperature range of 80° to 300°C and under equilibrium water vapor pressure. Below 200°C and various pressures of H_2O and CO_2, stevensite was obtained. Caillere, Henin, and Esteoule[5] prepared a mixture of two to four grams silica gel and two liters of magnesium acetate of con-

centration 0.02 N to 2 N and pH of 8.0, 8.6, and 8.9. After boiling the above mixture for one month, the product was found to be talc and stevensite.

The present work is restricted mainly to the systems $MgO-SiO_2-H_2O$ and $MgO-Al_2O_3-SiO_2-H_2O$ under alkaline conditions and over the temperature range of 25° to 200° C. Particular attention is focused on the chain structure clay minerals, attapulgite and sepiolite. Attapulgite is used extensively in industry. One of the largest commercial deposits in the world is located in southeastern United States, particularly in the states of Georgia and Florida.

Although the molecular structures of attapulgite and sepiolite have been carefully studied by Bradley,[6] Nagy and Bradley,[7] and Brauner and Preisinger,[8] these are, among the clay minerals, the least understood.

The stability of attapulgite and sepiolite in water and in $MgCl_2$ and $AlCl_3$ solutions was studied in order to determine the temperature range at which these two minerals, in equilibrium with the solutions, may exist. The solubility values of the two minerals in water, at room temperature, were used to calculate the activity product constant. Their standard free energies of formation were determined using the Nernst equation. The purpose of determining the activity product constant and the standard free energy of formation was to locate the concentration boundaries, including the hydrogen ion concentration, at which these minerals exist when in equilibrium with the solution. In addition, the relative stability compared to the other minerals may be obtained from the above calculation. The kinetics of acid dissolution was deter-

mined at four different temperatures for attapulgite and at one temperature for sepiolite. For both minerals, the reaction order with respect to the residual metal ions concentrations as well as with respect to acid concentration was obtained. The reaction rate constants of Mg, Al, and Fe ion contents in the clay were compared. In addition, the reaction rate constants of Mg ions in both attapulgite and sepiolite were compared and their relative resistance to acid weathering was determined. A reaction model for these two minerals was suggested. Using the reaction kinetics data for attapulgite at four different temperatures, the activation energy of acid dissolution was determined for Mg, Al, and Fe ions. Information was obtained from the acid dissolution experiment about the purity of the materials as well as about their molecular structure. Attempts were made to reconstitute the clay residue at different stages of acid digestion. Also, attapulgite was reacted with Mg ions, and the x-ray diffraction intensity of the 10.5 Å spacing of the product was compared with the untreated attapulgite.

Other methods of clay synthesis tried were the reaction in solution of Mg-Al-SiO_2 and the reaction of Mg-Al double hydroxides with an aqueous silica solution.

Solutions containing $MgCl_2$, $AlCl_3$, and SiO_2 of various compositions were prepared. The pH of the solutions was varied and the reactions were carried out at different temperatures. The reaction products were checked by x-ray diffraction, chemical analysis, and some by electron microscope.

Double hydroxides varying in composition from pure $Mg(OH)_2$ to pure $Al(OH)_3$ were prepared by adding Na_2CO_3 solution to a solution con-

taining a mixture of $MgCl_2$ and $AlCl_3$ at a pH of 10 and the double hydroxides were dialyzed with distilled water. The purpose of preparing the double hydroxides was to preorganize the octahedral layer; this was then reacted with aqueous silica solution at temperatures between 25° and 200° C. The products were examined by x-ray diffraction.

In addition to the above, many of the hypotheses concerning the origin of attapulgite and sepiolite were examined. These hypotheses will be presented in detail in Chapter II, but brief examples are mentioned below.

Kerr,[9] Reynolds,[10] and Bonatti and Joensuu[11] maintained that attapulgite is formed by the alteration of montmorillonite. Parry and Reeves[12] suggested that sepiolite is formed by the alteration of montmorillonite. Heystek and Schmidt,[13] Loughnan,[14] and Rogers, et al.[15] reported that attapulgite and sepiolite originated from the weathering of basalt, with montmorillonite as the intermediate weathering product. Longchambon[16] stated once that attapulgite was formed by the alteration of pyroxenes and amphiboles, but in a later paper[17] he proposed that attapulgite was derived from sepiolite by isomorphous substitution of aluminum for magnesium. Lapparent[18] stated that sepiolite is formed by the action of magnesium-rich solutions upon siliceous gels in the presence of lime, while McClellan[19] proposed that attapulgite is formed by the action of high magnesium sulfate solution from springs on siliceous sediments.

CHAPTER II

LITERATURE REVIEW

Synthesis of Clays

General Studies

Much work has been expended on the synthesis of clay minerals. The following is a representative cross section. Noll[20,21] is believed to be the first to have studied with modern methods of phase identification the systems Al_2O_3-SiO_2-H_2O and MgO-Al_2O_3-SiO_2-H_2O. In the system Al_2O_3-SiO_2-H_2O, Noll[20] heated at temperatures ranging from 250° to 500°C varying amounts of alumina and silica in a pressure bomb with a constant percentage of water. His data show that, with a molecular ratio Al_2O_3:SiO_2 of greater than 1:2, kaolinite and boehmite are formed up to 400°C, and an unidentifiable phase develops at 500°C. With a ratio of 1:2, only kaolinite is formed up to 350°C; between 350°C and 400°C, kaolinite, pyrophyllite, and boehmite are formed; and at 500°C, kaolinite and boehmite disappear, with only pyrophyllite and an unidentifiable phase formed. At a molar ratio Al_2O_3:SiO_2 of 1:4, kaolinite is the only crystalline phase up to 350°C, and between 400°C and 500°C pyrophyllite is the only phase developed. With molar ratio Al_2O_3:SiO_2 less than 1:4, the results of the synthesis are the same as when the ratio is exactly 1:4, except that amorphous silica appears at all temperatures. Noll[21] used temperatures between 300° and 400°C to study the system $(CaMg)O$-$(K_2Na_2)O$-Al_2O_3-SiO_2-H_2O. In each case, the bomb was 35 percent filled

with water and the pressures developed were 87 atmospheres at 300° C and 300 atmospheres at 400° C. As alkalies or alkaline earths are added to a mixture of composition Al_2O_3:4 SiO_2, smectite forms in increasing amounts at the expense of kaolinite. A concentration of about 0.2 mole of (CaMg)O or (Na_2K_2)O per mole of alumina with an Al_2O_3:SiO_2 molar ratio of 1:4 appears to be the optimum for the formation of smectite. At slightly higher concentrations, with MgO as the alkaline earth, smectite is still the phase formed. At higher Na_2O concentrations, analcime is formed, and at moderately higher K_2O concentrations, muscovite is formed.

A potash feldspar is formed at very high K_2O concentrations with an Al_2O_3:SiO_2 ratio of 1:4. At very high concentrations of MgO with the same Al_2O_3:SiO_2 ratio, talc and then serpentine is formed plus kaolinite or pyrophyllite instead of smectite. Pyrophyllite rather than smectite is the phase formed if the temperature is above 400° C.

Noll showed that kaolinite rather than mica is formed in an acidic medium with K_2O.

Yang[1] studied the reactions in the ternary system MgO-SiO_2-H_2O over the temperature range 100° to 300° C and found only two phases. Under conditions from 100° to 200° C and from atmospheric to 20,000 psi pressure and regardless of the initial MgO/SiO_2 ratio, the predominant magnesium silicate product was found to have a MgO/SiO_2 ratio of 1.5. In the range 200° to 300° C and from 210 to 20,000 psi, two stable phases, 3 MgO · 2 SiO_2 2 H_2O(I) and 3 MgO · 4 SiO_2 · H_2O(II), were observed. In this case, the favored phase was determined by the molar ratio of MgO/SiO_2 of the reaction mixture at initiation. The physical and chemical

properties of phases (I) and (II) resembled those of serpentine and talc, respectively. Two different morphologies were observed in electron micrographs of phase (I). From 100° to 160°C it occurred as crumpled foils, and at 170°C fibrous crystallites which resembled the natural asbestos mineral chrysotile appeared at the expense of the foils.

Henin, Caillere and their collaborators[22] have, for a number of years, performed syntheses at low temperatures using very dilute solutions of silicate and metal hydroxides which form a "brucite" layer structure. They succeeded in synthesizing trioctahedral minerals and considered that sheets of silica tetrahedra became attached to the brucite layers forming 2:1 type minerals at high pH where more silica was available and 1:1 type minerals at a lower pH with less silica available. The transformation of dioctahedral minerals, however, appeared to be exceptionally difficult.

De Kimpe, Gastuche, and Brindley[23] reported that the synthesis of aluminum and magnesium silicates had been carried out at low temperatures and normal pressures. With aluminum, a gel phase is abundant and identification of the crystals is possible only by electron diffraction; with magnesium, the yield in crystals is much higher and x-ray identification is possible. It is shown that the properties of the gels influence the type of crystals synthesized. The main factors are pH, salt concentration, and the ratio of aluminum or magnesium content to the silica content. For aluminum, the change from six-fold to four-fold coordination increases with pH. Kaolinite has been identified at low pH and mica-like structures at high pH. Serpentine minerals have been

obtained in an intermediate pH range. The better yield of magnesium-bearing minerals may be attributed to the six-fold coordination of this cation.

Further investigations by De Kimpe, Gastuche, and Brindley[24] showed that kaolinite was produced when the pH remained constant at about 1.5. The reaction was conducted holding 0.1 g gibbsite and 0.2 ml ethyl silicate at 170-175° C for ten days. Using Ludox SM silica gel instead of ethyl silicate produced the same results. In addition, kaolinite was synthesized at room temperature from dialyzed alumina gel and dialyzing silica solution. However, kaolinite could not be detected by x-ray diffraction and was detectable only from the electron microscope data.

Caillere, Esteoule, and Henin[25] studied the formation of trioctahedral silicates by the reaction of silico-alumina gel of $SiO_2:Al_2O_3$ with a molar ratio of 0.5-4 with magnesium acetate solution having a concentration between 0.1 N and 2 N. In some experiments, electrolytes of NaCl, KCl, and $CaCl_2$ of 2.0 N concentration were used. According to Caillere, et al., electrolytes such as NaCl and KCl were found to act as catalyst. The reaction temperature was held at 80° C. Bertherine is formed when the Mg concentration is 1.0 N or above. With low Mg concentration of the order of 0.1 N, saponite is formed. The pH of the solution was held at about 6.5 in order to prevent rapid precipitation of magnesium. They found the gel reaction to be considerably faster than the solution reaction.

Caillere, Henin, and Esteoule[5] in another study prepared two to four grams of silica gel and two liters of magnesium acetate with con-

centrations from 0.02 N to 2 N and pH's of 8.0, 8.6, and 8.9 with and without NaCl. The above mixture was boiled for one month in a flask connected to a reflux condenser in order to hold the volume constant. The product was found to be talc and stevensite in the absence of NaCl. In the presence of NaCl, a gel is formed in addition to talc and stevensite.

The effect of impurities on the synthesis of clay was studied by several investigators. According to Gastuche and Herbillon,[26] the anionic impurities disorder the Al-octahedral layers. Fripiat, Leonard, and Barake[27] found that cationic impurities strongly affected the silica-gel framework.

Iiyama and Roy[28] prepared a gel of composition $\frac{x}{2}$ Na_2O · 3 MgO · $\frac{x}{2}$ Al_2O_3 (4-x) SiO_2, with x varying from 0 to 1.0. This gel was heated to from 400° to 800°C and water vapor pressures of 1000 atmospheres for several days. They reported that heterotypic phases of talc and saponite were formed on the low Na side and on the high Na side was formed saponite and a 10 Å layer mineral believed to be Na-mica.

Granquist and Pollack[29] reported the synthesis of a randomly interstratified layer lattice silicate (a heteropolytypic montmorillonoid) from a starting slurry of diatomaceous earth and bayerite in an aqueous solution of NaOH. The synthesis was carried out for varying reaction times (0-72 hours) at 279° and 300°C and the water vapor pressure corresponded to those temperatures. They suggested that the synthesis occurs in three steps: solution of the solid reactants, nucleation of the layer lattice, and growth of these nuclei to the final crystalline product. The growth step is sufficiently rapid so that the solution

and/or nucleation steps become rate-controlling.

Poncelet and Brindley[30] prepared Al-OH-montmorillonite by adding solutions of 0.1 N NaOH and 0.2 M $AlCl_3$ dropwise, while stirring vigorously, to 0.4 percent Na-montmorillonite suspensions. A mixture containing 1500 meq Al per 100 g clay and with a NaOH:Al ratio of about 2.7 forms Al-OH polymers which are taken up by the montmorillonite in almost sufficient amounts to form complete gibbsite-like layers between the montmorillonite layers. When this material was treated with 1 N HCl (pH 4.8) at 220° C for seven days, the Al-OH-montmorillonite yielded abundant well-crystallized kaolinite. A major difference between the above results and those reported earlier is that kaolinite was obtained without the use of a strongly acid medium. A kaolin mineral was always detected in experiments conducted at 220° C for seven days even with distilled water.

De Kimpe and Fripiat[31] synthesized kaolinite starting from various zeolites, erionites, mordenites, and analcite. In the first stage, the samples were treated with 0.1 N HCl at room temperature. Subsequent hydrothermal treatment under acid conditions (0.1 N HCl) for ten days at 175° C or 230° C gave kaolinite. They mentioned that at high temperature and pressure, where the temperature coefficient of the reaction is very favorable, almost any appropriate mixture of hydrated aluminas and silicas (molar ratio of Al:Si equal to one) would produce kaolin mineral under acidic conditions.

Studies Concerning Chain Structure Clays

Mumpton and Roy[32] concluded that hydrothermal studies have failed to yield synthetic attapulgite or sepiolite in the system $MgO-Al_2O_3-SiO_2-$

H_2O. They prepared synthetic gel mixtures with the approximate compositions of an average attapulgite and an average sepiolite (minus CaO). The oxide ratios of these two amorphous starting gels were as follows:

Attapulgite gel, 69.0, SiO_2: 9.2, Al_2O_3: 21.8 MgO

Sepiolite gel, 59.6, SiO_2: 2.3 Al_2O_3: 38.1 MgO

At approximately 200°C underwater pressures of from 10,000 to 25,000 psi in tests varying from a few hours to three weeks in duration, these gels yielded only saponite and montmorillonite. Above 350°C, talc, silica, and chlorite phases were found to be stable.

Since all efforts to crystallize attapulgite and sepiolite from synthetic starting material failed, Mumpton and Roy suggested that one possible conclusion is that these minerals are not stable phases in this system in the presence of excess water.

Siffert[2] and Siffert and Wey[3] reported that in alkaline medium at ordinary temperature magnesium reacts with a monomolecular silica solution to form fibrous clay of the sepiolite type. They prepared silica-magnesium chloride solutions of several compositions and adjusted the pH with sodium hydroxide. A molar ratio, SiO_2:MgO, of 1.5 and final pH of 8.8 is recommended as the most favorable solution for synthesis of sepiolite. The mixtures were left at room temperature for three weeks. The products obtained were found to be poorly crystallized, but they were identified by differential thermal analysis, electron microscopy, and electron diffraction.

Preisinger[4] reported that an attempt to synthesize sepiolite in the system $MgO-SiO_2-H_2O$ under confined pressure within a temperature range of 80°-300°C did not succeed. In the system $MgO-SiO_2-H_2O$ with a

MgO:SiO_2 ratio of 2:3 heated below 200°C and various pressures of H_2O and CO_2, stevensite was obtained.

Esteoule[33] mentioned that by reacting, at 95-100°C, the alumina-silicate gels with very dilute solutions of magnesium acetate (0.01 N), in the presence of 2.0 N NaCl, a fibrous product with the characteristics of attapulgite was obtained. However, he admitted that the product was practically amorphous to x-ray and it was not possible to identify the product with certainty using the classical methods of mineralogy. When more dilute Mg acetate (0.002 N) was used, very few fibers were obtained. More concentrated Mg acetate produced phyllites similar to that of saponite.

Garrels and Mackenzie,[34] and Wollast, Mackenzie, and Bricker[35] have found that the reaction at room temperature of sodium metasilicate with sea water produced a hydrated magnesium silicate similar to sepiolite in structure and composition. They also reported that the addition of SiO_2 to $MgCl_2$ solution resulted in the precipitation of sepiolite. For both cases, slightly alkaline conditions were used (pH about 8.0). However, Wallast, Mackenzie, and Bricker admitted that conventional x-ray diffraction was not satisfactory for determining the nature of the precipitate because the product was so poorly crystallized. Therefore, other methods of identification were used such as infrared spectrophotometry and electron microscopy.

Free Energy of Formation

Keller, Balgord, and Reesman[36] and Reesman and Keller[37,38] conducted extensive work on the aqueous solubility of a large number of

minerals, including kaolinite and montmorillonite. They calculated the standard free energy of formation from the activity-product constant and from the documented standard free energies of formation of the products of the chemical and the dissolution reactions.

Using the solubility data in water at room temperature, Kittrick[39] calculated the standard free energy of formation of kaolinite. He reported that ΔF_f° ranged from -902.5 to -903.8 kcal/mole depending on the crystallinity of the clay. Kittrick found that, in a general way, as the crystallinity of the kaolinites decreased the ΔF_f° became increasingly positive. Although the dissolution equation is somewhat different from that used by Reesman and Keller,[38] his ΔF_f° results are within the range given by Reesman and Keller.

Hostetler and Christ[40] determined the solubility data of chrysotile in water at 90° C and atmospheric pressure. Then, using the necessary thermochemical data, they calculated the activity-product constants and the free energies of formation of chrysotile for temperatures ranging from 0° C to 200° C. The standard free energy of formation for chrysotile was found to be -964.92 kcal/mole of $Mg_3Si_2O_5(OH)_4$.

Garrels and Mackenzie[34] prepared magnesium silicate by adding sodium metasilicate to sea water. They calculated the solubility product constant to be approximately 10^{-24}.

Wollast, Mackenzie, and Bricker[35] reported the synthesis of sepiolite and determined the concentration of the solution in equilibrium with the synthesized product. They calculated the standard free energy of formation for dehydrated sepiolite to be -903 ± 0.5 kcal/mole of $Mg_2Si_3O_8$.

Kinetics of Acid-Dissolution

It is believed that Brindley and Youell[41] were the first to determine the amounts of octahedral and tetrahedral aluminum in silicate minerals using the acid attack technique. They digested magnesium chlorite (penninite) with a considerable excess of 10 percent HCl at constant temperatures for various time intervals. The percentages of Mg, Fe, and H_2O extracted were found to follow the same curve when plotted against time; in the case of aluminum, the extraction rates are similar up to about 47 percent, but thereafter they proceed very much more slowly. Brindley and Youell concluded that octahedral aluminum is represented by the first part of the curve, whereas the second part of the curve represents tetrahedral aluminum. Their results were found to agree closely with those given by the structural formula.

More detailed studies of the kinetics of acid dissolution were made by Osthaus.[42,43] He digested several montmorillonites and a nontronite with HCl at constant temperatures for various periods of time. Rate of dissolution curves were obtained by plotting the logarithm of the percent of the residual ions against time. In general, the dissolution curves were straight lines or curves that could be resolved into two straight lines. From the interpretation of the dissolution curves, it was possible to determine the amount of cations in octahedral and tetrahedral coordination.

The dissolution of the ions from the clay lattice, determined at several temperatures in one sample and at two acid concentrations in another sample, was found by Osthaus to be in agreement with chemical kinetics principles and to be a first-order reaction with respect to

both residual ion concentration and to acid concentration. In addition, he found that the Mg, Al, and Fe ions in the octahedral layer have approximately the same reaction rate. Using Arrhenius' law, the activation energy of acid dissolution was found to be between 17 and 18 kilocalories per mole. This was found to be true for both octahedral and tetrahedral ions.

Granquist and Sumner[44] studied the various physical properties of an acid-treated Texas bentonite as a function of treatment time. They also found pseudo first-order kinetics. Hydrochloric acid of 10 percent concentration was used in an amount calculated to be ten times that required for complete dissolution of all cationic components of the crude material. Treatments were carried out primarily at 103° C, but some data were obtained at 67° C.

In calculating the reaction rate, a new approach based on the x-ray intensity of the 17 Å spacing rather than the results of chemical analysis was used by Granquist and Sumner. Based on this new method, it was found that the reaction rate was higher than that calculated from chemical analysis. Using the kinetics data of two different temperatures, the activation energy was calculated to be 7.27 kcal/mole. Two different models were examined and it was concluded that a cylindrical model and an edge attack best fit the experimental data.

Gastuche[45] studied the kinetics of acid dissolution of biotite. He examined the effect of the amorphous silica formed during the acid dissolution in limiting the diffusion of the dissolved cations and of hydrogen ions at the interface. Gastuche found that the acid dissolution of biotite is a tridimensional process which fits a first-order

reaction with respect to the HCl concentration. At low temperatures, no limitation due to the diffusion process is noticeable; however, at 100°C the reaction along the c-axis is hindered by a diffusion mechanism. The activation energy by the acid dissolution of biotite was calculated by Gastuche to be about 10 kcal/mole.

Origin of Attapulgite and Sepiolite

The origin of attapulgite and sepiolite minerals is at present controversial. Although many hypotheses have been proposed to explain the origin of these two clay minerals, no systematic understanding of their origin has been published.

Longchambon[16] attributed the origin of attapulgite to the alteration of pyroxenes and amphiboles, and in a later paper[17] he proposed that attapulgite was derived from sepiolite by the isomorphous substitution of aluminum for magnesium. Lapparent[18] stated that sepiolite is formed by the action of magnesium-rich solutions on siliceous gels in the presence of lime. Kerr[9] suggested that attapulgite from Georgia was formed by the alteration of montmorillonite minerals. Caillere and Henin[46] believed that certain sepiolites are secondary products resulting from the weathering of enclosing serpentine bodies. Sepiolite, resembling metacolloidal asbestos, has been reported by Serdyuchenko[47] to occur in silicified serpentinites accompanied by veinlets of quartz, opal, and calcite, replacing older carbonate host rock. Heystek and Schmidt[13] suggested that attapulgite in the Springbok Flats, Transvaal, was formed by the weathering of basalt, with montmorillonite as the intermediate weathering product. The amount of attapulgite in any one

weathering zone of this basalt can be correlated roughly with the quantity of carbonate present. Rogers, Martin, and Norrish[15] proposed that tropical weathering of basalt in Queensland, Australia, released alkali and alkaline earth metals and silicon. Calcium, magnesium, and silicon from basalt appear to have accumulated in lakes and precipitated out as dolomite, sepiolite, and chert. Stephen[48] believed that the attapulgite of the Shetland Isles was formed by the alteration of syenite by the action of hydrothermal solutions containing magnesium. Mumpton and Roy[32] reported that attapulgite and sepiolite associated with weathered pyroxenes and amphiboles are quite likely to have been formed by the groundwater alteration of these chain-structure minerals at low temperatures. The reason for the formation of these minerals rather than montmorillonite or talc may be ascribed to structural control from the parent amphibole or pyroxene. Loughnan[14] suggested that attapulgite and sepiolite in the Redbank plains, Queensland, Australia, was formed by the reaction of weathered basalt with magnesium-rich water. He suggested the following transformation sequence:

$$\text{Montmorillonite} \xrightarrow{Mg} \text{Attapulgite} \xrightarrow{Mg} \text{Sepiolite} \xrightarrow{Mg} \text{Dolomite}$$

Demangeon and Salvayre[49] believed that attapulgite in duMont-Perdu, Spain, was formed from magnesium (derived from dolomite), silica (derived from quartz), and aluminum (derived from other clay minerals). Shabayeva[50] reported that attapulgite from southeastern Turkmenia is a sedimentary product and was produced in a weak alkaline medium by the reaction of magnesium ions and silica released by the decomposition of

volcanic ash. Reynolds[10] stated that attapulgite and sepiolite from Florida were formed by the alteration of montmorillonite. Millot, Lucas, and Wey[51] suggested that montmorillonite, attapulgite, and sepiolite in North Africa were formed by a process they termed neoformation. Siliceous and argillaceous neoformations consist of organization and combination of silica tetrahedrons with such ions as aluminum and magnesium in an alkaline environment. Buie and Gremillion[52] and Gremillion[53] proposed that attapulgite in southeastern United States is an alteration product of volcanic ash which accumulated and decomposed in a marine environment. The presence of limestone, phosphorite, and unoxidized sulfur species indicates that the environment was an alkaline and reducing one. The pH at the time of formation must have been at least 7.8. McClellan[19] postulated that attapulgite in the Florida-Georgia region was formed by the action of a high magnesium sulfate spring solution on the siliceous sediments which consist of siliceous diatom valves and possibly the detrital clay materials. The carbonates associated with the original site of attapulgite formation are needed to protect the attapulgite from acid groundwater attack. Parry and Reeves[12] believed that the sepiolite found at Mound Lake was formed from montmorillonite as a result of exposure to alkaline lake brine rich in magnesium. The usual pH in the lake is 8.0. They thought that the relative scarcity of montmorillonite in sepiolite-bearing strata suggested that montmorillonite was the source material. Bonatti and Joensuu[11] suggested that attapulgite in deep sea sediment from the Barracuda Escarpment in the western Atlantic was formed by the hydrothermal alteration of montmorillonite and the action of magnesium-rich

solutions. They suggested the following possible equation

Montmorillonite + SiO_2 +

+ (Ca and Mg in solution) $\longrightarrow$ Attapulgite + Clinoptilolite.

CHAPTER III

EQUIPMENT AND PROCEDURE

Clay Synthesis

Room Temperature

A mixture of the proper composition of the system $Mg\text{-}Al\text{-}SiO_2\text{-}H_2O$ is placed in polypropylene containers of about 800 ml capacity, tightly capped and aged. At the end of the reaction time, the mother solution is analyzed and the residue is checked by x-ray diffraction.

The following analyses were performed on the mother solution.

1. The hydrogen ion activity was measured using a Model 12, pH meter manufactured by Corning Glass Works, Cambridge, Massachusetts.

2. Magnesium, aluminum, and other cations were analyzed in solution using the atomic absorption spectrophotometer, Model 303, manufactured by Perkin-Elmer, Norwalk, Connecticut. The theory of atomic absorption spectrophotometry is briefly as follows. A sample is converted into an atomic vapor, usually by a flame, and irradiated by the light from a source having emission lines identical with those of the metal being sought. The absorption of the light by the vaporized sample is related to the concentration of the desired metal in it.

3. Silica was determined using the yellow silicomolybdate method of Govett.[54] The absorbance was measured at 430 mμ with a Spectronic 20 instrument manufactured by Bausch and Lomb, Rochester, New York. For silica concentrations above 100 ppm SiO_2, the determination was made

with the atomic absorption spectrophotometer.

The reaction residue was washed and centrifuged several times. A Model UV centrifuge, manufactured by the International Equipment Company, Needham Heights, Massachusetts, was used. Afterwards, the residue was heated overnight in the oven at about 80° C and then a slide was made for x-ray diffraction. The x-ray machine employed was manufactured by Philips Electronic Instruments, Mount Vernon, New York.

Electron micrographs of several residues were made by the staff of the Georgia Institute of Technology Engineering Experiment Station.

Hydrothermal Conditions

In the first part of these experiments, the reaction mixture was heated in a stainless steel, type 316, pressure reaction apparatus, stirrer type, catalog No. 4511, and manufactured by Parr Instruments Company, Moline, Illinois. However, due to excessive corrosion, the use of this apparatus was discontinued. The corrosion is believed to have been due to the fact that some parts in the apparatus had not been made of stainless steel. Subsequently, most of the experiments were performed using pressure bombs. The pressure bombs were made from Schedule 40, one inch nominal diameter nickel and type 316 stainless steel pipes, approximately seven inches long. One inch caps were fitted tightly to the pipes using Teflon tape. Mixtures of the proper composition were transferred into the pressure bombs, which were then placed in an oven or a furnace and heated to the desired temperature. Following heating, the same analyses as those performed for the clay synthesis experiments at room temperature were performed.

In addition to the clay synthesis experiments, the pressure bombs

were used in the experiments for locating the stability field of attapulgite and sepiolite.

Free Energy of Formation

The procedure used in this experiment was similar to that of Keller, et al.,[36] as revised by Reesman and Keller.[38] Ten grams of fine powdered clay sample (particle size less than one micron) was washed several times with distilled water. Then 100 ml of distilled water was added to each clay sample in a polypropylene beaker and tightly capped. The mixture was stirred periodically using a magnetic stirrer. After standing at room temperature for a period ranging from seven to thirty days, the mixture was centrifuged (International Centrifuge, Model UV) at 2000 rpm for several hours until clear solution was obtained. The clear solution was then separated and centrifuged again at 15,000 rpm for about one hour using a Model SS-3, automatic superspeed centrifuge, manufactured by Sorval, Inc., Norwalk, Connecticut. Finally, the concentration of soluble material and the pH of the clear solution were determined.

Silica was determined by the yellow silicomolybdate method of Govett[54] and magnesium by its atomic absorption spectra. Aluminum in very low concentration was determined by following essentially the 8-hydroxyquinoline method of Riley and Williams.[55] Methyl isobutyl ketone was employed as the organic solvent instead of chloroform. The absorbance was measured at 390 mμ using the Spectronic 20. The yellow compound produced is very sensitive to light. However, after about five minutes, the absorbance decreases to a low level and stays constant for

several hours thereafter. The absorbance of both the standard and the unknown solutions was measured during that time. The solutions analyzed did not contain interfering elements; therefore, the preliminary treatment outlined in the standard method to remove these elements was omitted.

Kinetics of Acid-Dissolution of Attapulgite and Sepiolite

The method used in this investigation was essentially that of Osthaus.[43] The clay specimens were ground and the particles smaller than one micron in diameter were separated with the centrifuge, washed several times with distilled water, and then dried at room temperature. This material was left at room temperature for a sufficient time to assure its equilibrium with air. One gram samples were employed for each test. To avoid the effects of changing humidity, samples sufficient for all the tests were weighed within a short period of time. The one gram samples were then transferred to a 500 ml round-bottomed Pyrex flask. Next, 200 ml of hydrochloric acid, which was heated to the reaction temperature, was added and the flask was quickly connected to water-cooled reflux condensors by ball and socket ground glass joints. The bulb section of the flask was submerged in a constant temperature water bath for various periods of time. The water bath temperature was controlled by a coil of copper tubing which was connected to a Lauda constant temperature circulator, Model K-2, manufactured by Brinkmann Instruments, Westbury, New York. Uniformity of the bath temperature was achieved by using a magnetic stirrer, while the water lost by evaporation from the bath was kept constant by adding water dropwise from a large water jar using a stopcock. At the end of each digestion period,

the flask was removed and quickly cooled with ice. The clay-acid suspension was centrifuged and then filtered; the filtrate was retained for chemical analysis. For about 50 percent digestion or less, the filtrate was analyzed for soluble Mg, Al, and Fe. The amount of each of the residual ions was calculated by subtracting the percent soluble from the total percent in the sample. For considerably greater than 50 percent digestion, it was advantageous to determine the small amounts of residual Mg, Al, and Fe directly from the insoluble residues. The attapulgite was digested in 2.5 N and 5.0 N hydrochloric acid. Two hundred milliliters of 5.0 N HCl is about 85 times that required for complete digestion of the cations in 1.0 g attapulgite. Hydrochloric acid having a concentration of 1.0 N was used to digest the sepiolite. This is equivalent to about 19 times that required for the complete digestion of the cations. In solution, Mg, Al, and Fe analyses were made with an atomic absorption spectrophotometer. For analysis of these elements in the residue, the sample was first brought into solution by fusion with $LiBO_2$ and then dissolved in four percent HNO_3. The method of Suhr and Ingamells[56] was followed except that the dissolving solution (four percent HNO_3) did not contain $Co(NO_3)_2$.

CHAPTER IV

RESULTS AND DISCUSSION

Clay Synthesis

Reaction in Solution

Solutions containing Mg-Al-SiO_2 of various ratios and concentration levels were prepared. Calcium and ferric ions were used in some tests in addition to Mg-Al-SiO_2. In most cases, $MgCl_2$, $AlCl_3$, and monomolecular silica solution were employed. However, $MgSO_4$, $Na_3[Al(C_2O_4)_3]$, and silica solution "Ludox SM" were also used in some experiments. No difference was detected due to the form of the initial components.

Results are listed in Tables 1 and 10 (Appendix B). In Table 10 the initial components were reacted at room temperature. For most of the solution compositions, pH of 7, 8, 9, 10, and 11 were employed. The mixtures were aged for at least 30 days, the solutions were analyzed, and the residue products checked by x-ray diffraction. In addition, the mixtures were left for at least one year and the residue products were again examined by x-ray diffraction. The chemical composition of the products was calculated indirectly by determining the final composition of the solutions in contact with the residue. Evidence indicates that most of the residue products were not single chemical compounds, as shown by their x-ray diffraction patterns as listed in Table 10. At room temperature, a large number of the products was found to be amorphous to x-ray. In general, the Mg-Al double hydroxides were formed

Table 1. Reaction Data for Mg-Al-SiO_2 System

Test No.	Initial Solution ppm			pH		Temperature °C	Reaction Time Days	X-ray Identification of Reaction Product
	Mg	Al	SiO_2	Initial	Final			
100	988	54	51	9.0	7.6	80	3	broad peak~8.84 Å
100A	988	54	51	9.0	--	200	6	double hydroxides
101	988	54	51	10.0	9.2	80	3	double hydroxides and brucite
102	988	54	51	11.0	10.1	80	3	double hydroxides and brucite
108	50	--	167	10.5	--	200	7	serpentine~ 7.9 Å
109	50	--	179	10.0	--	200	3	saponite
110	100	--	180	11.0	9.4	25	21	montmorillonoid
111	100	--	180	11.0	--	80	7	montmorillonoid
112	200	--	360	11.0	10.5	110	5	montmorillonoid
113	200	--	360	11.0	10.2	150	7	serpentine~ 8.5 Å
114	1000	--	1800	11.0	10.3	200	5	serpentine~ 7.5 Å
115*	900	1000	9000	7.0	5.2	110	7	amorphous
116*	900	1000	9000	10.0	6.9	110	7	amorphous
117*	900	1000	9000	7.0	4.3	150	7	amorphous
118*	900	1000	9000	8.0	4.9	150	7	amorphous

*Nos. 115-118 contained about 1.3 N NaCl.

from solutions with high Mg/Al ratio and high final pH. The minimum final pH of the solution needed for the formation of double hydroxides was found to be approximately 8.0. Also, the crystallinity of the double hydroxides seemed to increase with the increase in pH, as indicated by the x-ray intensity of the double hydroxide peak.

Table 10 shows that crystalline clay minerals were formed in relatively few runs. The x-ray pattern of the reaction residue from Test No. 27 showed a very weak peak characteristic of attapulgite. The electron micrograph of this product showed some fibrous material as may be seen in Figure 1. However, complete identification of the product was not possible. Tests No. 88 to 92 were similar to Nos. 83 to 87 except that the solutions also contained 22 ppm Fe^{3+}. The products of both of the above groups were found to be essentially similar. Tests No. 103 to 107 contained Ca^{2+} in addition to the Mg-Al-SiO_2 components. The results showed that the presence of Fe^{3+} or Ca^{2+} did not have any effect on the formation of clay minerals.

Many of the mixtures produced a poorly crystallized montmorillonite-like clay which is given the name of montmorillonoid. This material produces broad peaks in the 10 to 30 Å region. The material called double hydroxide has peaks ranging from 7.5 Å to 8.3 Å. The better crystallized material showed at least three 00ℓ reflections. Some of this 7.8 Å precipitate could be a serpentine-like material, although in most instances the SiO_2 content of the product is too low.

Montmorillonoids formed only in the pH range seven to nine. The magnesium content of these reaction products was zero, or very low. Double hydroxides formed in the pH range nine to eleven. In general,

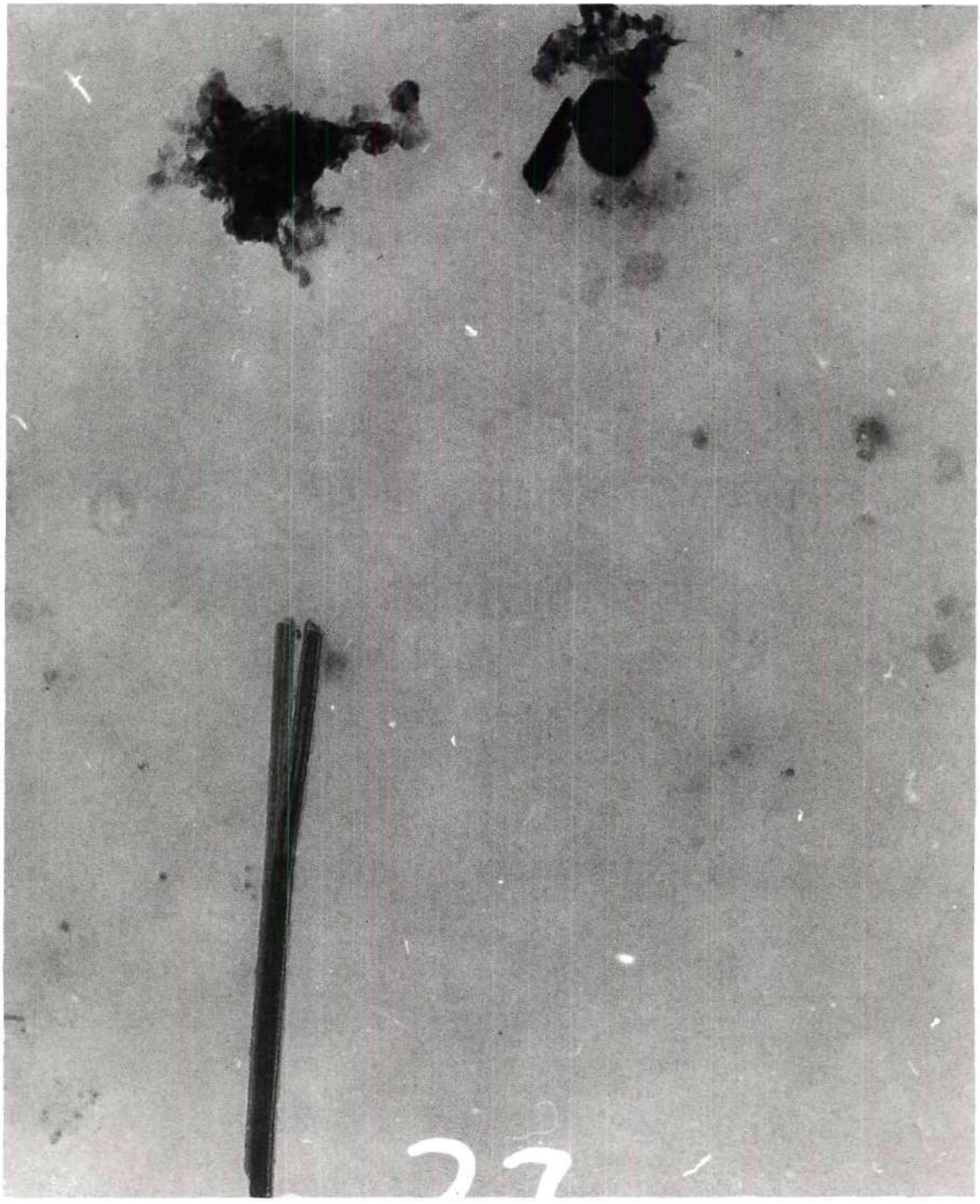

Figure 1. Electron Micrograph of Reaction Residue from Test No. 27

the thickness (by x-ray) of the layer increased as the Mg/Al ratio of the product increased. Also, as the pH increased for a given starting composition, the Mg content of the reaction product increased, and the Al content decreased; the Si content appeared to be independent of pH. Only a few of the reaction products had an SiO_2 content as large as attapulgite.

Table 1 lists the reaction data of Mg-Al-SiO_2 system at various temperatures. Test No. 100 residue gave an x-ray pattern with a broad peak of about 8.84 Å spacing and another sharper peak of about 5.0 Å spacing. The electron micrograph, as shown in Figure 2, revealed small fibrous material. This product could not be identified. Test No. 108 had a molar ratio SiO_2/Mg of about 1.35. In addition to serpentine, a weak peak thought to be characteristic of attapulgite was found in the x-ray pattern of this product. The electron micrograph of the product revealed fibrous-shaped material, as shown in Figure 3. However, since chrysotile (a form of serpentine) is also fibrous, attapulgite could not be positively identified.

Aluminum is required for the formation of saponite. In Test No. 109 a Pyrex beaker was used inside the pressure reaction apparatus. Therefore, it is believed that glass was the source of aluminum for the formation of saponite.

Tests No. 110-114, having a SiO_2/Mg molar ratio of about 0.7, represent the composition recommended by Siffert.[2] He reported the formation of sepiolite after aging this solution at room temperature for three weeks. However, in these experiments sepiolite could not be identified in the reaction product by x-ray diffraction. At room tem-

Figure 2. Electron Micrograph of Reaction Residue from Test No. 100

Figure 3. Electron Micrograph of Reaction Residue from Test No. 108

perature (Test No. 110), the reaction product was examined by x-ray diffraction and found to contain an 11 Å spacing which expands into about 15 Å upon saturation with ethylene glycol. Therefore, the product is a 2:1 layer silicate of the montmorillonite type. The same mineral was identified at 80°C (Test No. 111). Test No. 112 had a poorly crystallized reaction product at 110°C. A broad peak characteristic of a montmorillonite-type mineral was obtained. At 150°C (Test No. 113), a nonexpanding mineral was produced with a spacing at about 8.5 Å which did not collapse by heating overnight at 300°C. It is believed that this mineral represented a hydrated form of serpentine or, perhaps, a mixed-layer phase. Test No. 114 represented the reaction at 200°C. The product is a typical 1:1 layer silicate of the serpentine type having a spacing of about 7.5 Å.

Therefore, the results showed that for Mg-SiO_2 system under alkaline conditions and within the reaction temperature range of 25-200°C, lower temperatures favor the formation of 2:1 layer silicates while higher temperatures favor that of 1:1 layer silicates.

The solution composition of Tests No. 115 to 118 corresponds to that of attapulgite with a Mg/Al molar ratio of approximately one. The solution also contained 1.3 N NaCl. All the reaction products were found to be amorphous to x-ray.

Esteoule[33] prepared alumino-silica gel of composition: 30 percent H_2O, 32.7 percent SiO_2, 36 percent Al_2O_3, and 1.85 percent Na_2O by mixing intimately in a mortar, 9.6 grams $Na_2SiO_3 \cdot 5\ H_2O$, 3.1 grams aluminum basic acetate, and 7.5 grams aluminum nitrate. The product was washed thoroughly and centrifuged. He reported that, by reaction

at a temperature in the vicinity of 100°C, the alumino-silica gel with 0.01 N magnesium acetate solution in the presence of 2 N NaCl, yielded a fibrous product similar to attapulgite. In this work, alumino-silica gel was prepared using the method of Esteoule. Two portions of the alumino-silica gel were reacted with 0.01 N magnesium acetate solution containing 2 N NaCl under the following condition.

a. The initial pH was adjusted to 9.0 by adding CaO. The mixture was heated at 110°C in a pressure reaction bomb for 11 days. The final pH was 6.4.

b. The initial pH was 5.7. The mixture was heated at 150°C for seven days. The final pH was 4.8.

The residues from both tests were examined by x-ray diffraction and found to be amorphous.

Reaction of Mg-Al Double Hydroxides with Silica Solution

Feitknecht[57] and Feitknecht and Gerber[58] were the first to show that a large number of different layer lattice structures resulted from the combination of divalent and trivalent cation with similar ionic radii; they described the products as "double hydroxides." They prepared Mg-Al double hydroxides from their chlorides by adding sodium hydroxide to the solution and aging the material in the mother solution. Feitknecht and Gerber reported the ideal formula of the Mg-Al double hydroxides as 4 $Mg(OH)_2$, 1 $Al(OH)_3$, or 4 $Mg(OH)_2$, 1 AlO(OH). Mortland and Gastuche[59] prepared the mixed Mg-Al hydroxides from the corresponding chlorides aged in a dialyzed medium, achieving in this way a much better crystallization and a higher purity than did Feitknecht and Gerber. They found two double hydroxides. The first one is character-

ized by the higher magnesium content and has parameters slightly larger than the second species which was richer in aluminum. Mortland and Gastuche concluded that the pure double hydroxides have a molar ratio Mg/(Mg+Al) varying between 0.7 to 0.8. They reported that excess of Mg leads to crystallization into brucite while high Al samples contain bayerite.

The method of Mortland and Gastuche was followed in this work. Two solutions of 0.25 M $MgCl_2$ and 0.25 M $AlCl_3$ were mixed in the proper ratios. The pH was first adjusted to 10 by adding 4 N Na_2CO_3 solution. The gel was next centrifuged, then placed in cellulose bags, and dialyzed in distilled water at 60°C until free from chloride ions. The bath water was changed twice a day for about 30 days.

Dialyzed double hydroxides of composition varying from pure bayerite $Al(OH)_3$ to pure brucite $Mg(OH)_2$ were prepared. Examination by x-ray diffraction showed that the first-order parameter varied between from about 7.628 Å to about 8.191 Å, depending on the Mg content in the double hydroxides. The higher the Mg content, the larger the parameter.

Table 2 lists the reaction results of the double hydroxides with silica solution at temperature ranging between 25-200°C. At room temperature, the percent SiO_2 reacted depended on the composition of the double hydroxides. In general, the higher the Mg content in the double hydroxides, the higher the percent silica reacted. The results indicate that, in the Mg-Al-SiO_2 system, low Mg/Al ratios favor the formation of dioctahedral layer montmorillonite, whereas high Mg/Al ratios favor the formation of trioctahedral layer saponite. In the intermediate range,

Table 2. Reaction Data for Double Hydroxides with SiO_2

Test No.	Double Hydroxides Molar Ratio Mg/(Mg + Al)	Temperature °C	Reaction Time Days	X-ray Identification of Reaction Product
121	0.0 [$Al(OH)_3$]	25	90	poorly crystallized
122	0.0 [$Al(OH)_3$]	200	4	boehmite
126	0.144	25	90	poorly crystallized
127	0.144	110	15	poorly crystallized
128	0.144	150	7	poorly crystallized
129	0.144	200	5	montmorillonite and boehmite
131	0.233	25	90	poorly crystallized
132	0.233	110	7	poorly crystallized
133	0.233	150	7	poorly crystallized
134	0.233	200	7	montmorillonite and boehmite
136	0.306	25	90	poorly crystallized
137	0.306	110	7	poorly crystallized
138	0.306	150	7	poorly crystallized
139	0.306	200	5	montmorillonite
141	0.47	25	90	poorly crystallized
142	0.47	110	7	poorly crystallized
143	0.47	150	7	poorly crystallized
144	0.47	200	5	~7.25 Å serpentine and boehmite
146	0.52	25	90	poorly crystallized
147	0.52	110	13	poorly crystallized
148	0.52	150	7	poorly crystallized
149	0.52	200	3	~7.37 Å serpentine and boehmite
151	0.61	25	90	poorly crystallized
152	0.61	110	11	poorly crystallized
153	0.61	150	7	poorly crystallized
154	0.61	200	5	~7.5 Å serpentine and boehmite

Table 2. Reaction Data for Double Hydroxides with SiO_2 (Concluded)

Test No.	Double Hydroxides Molar Ratio Mg/(Mg + Al)	Temperature °C	Reaction Time Days	X-ray Identification of Reaction Product
156	0.714	25	90	poorly crystallized
157	0.714	110	11	poorly crystallized
158	0.714	150	7	poorly crystallized
159	0.714	200	10	saponite ?
161	0.805	25	90	poorly crystallized
162	0.805	110	19	poorly crystallized
163	0.805	150	7	poorly crystallized
164	0.805	200	5	unidentified ~4.65 Å
166	0.894	25	90	poorly crystallized
167	0.894	110	18	poorly crystallized
168	0.894	150	7	saponite
169	0.894	200	7	unidentified ~4.65 Å
171	1.0 [$Mg(OH)_2$]	25	90	2:1 layer silicate
172	1.0 [$Mg(OH)_2$]	110	14	2:1 layer silicate
173	1.0 [$Mg(OH)_2$]	150	7	2:1 layer silicate
174	1.0 [$Mg(OH)_2$]	200	19	~7.56 Å serpentine

serpentine was formed. Also, serpentine was formed in the Mg-SiO_2 system as shown in Test No. 174. It was noticed that the parameters of the serpentines formed are somewhat variable, depending on the composition of the reacting double hydroxides. The parameter increased with the increase in the Mg/Al ratio. For example, the serpentines formed in Tests No. 144 and 149 have parameters of approximately 7.25 Å and 7.37 Å, respectively, whereas the serpentine formed from pure $Mg(OH)_2$ has a parameter of approximately 7.56 Å as shown in Test No. 174. Tests No. 144, 149, and 154 produced boehmite in the reaction product in addition to serpentines. Therefore, the actual Mg/Al ratios in the serpentines are higher than the corresponding ratios of the reacting double hydroxides. Tests No. 164 and 169 revealed a reaction product with a spacing of about 4.65 Å. This product could not be positively identified.

Regions of Stability of Attapulgite and Sepiolite

Mumpton and Roy[32] reported that at temperatures as low as 200° C, under 20,000 psi water pressure, well crystallized attapulgites and sepiolites break down into well crystallized "expanding" montmorillonite and saponite structures. At temperatures higher than about 350° C quartz, talc, and chlorite phases appeared. The reactions can be represented by the following equations.

$$\text{attapulgite} \xrightarrow[7\text{-}21 \text{ days}]{200^\circ C,\ 20{,}000 \text{ psi}} \text{montmorillonite} \xrightarrow{350^\circ C} \text{silica} +$$

$$+ \text{talc or pyrophyllite} + \text{chlorite}$$

$$\text{sepiolite} \xrightarrow{200^\circ C} \text{saponite} \xrightarrow{350^\circ C} \text{talc} + ?$$

Since both attapulgite and sepiolite are low density minerals containing open channels in their molecular structure, their regions of stability might be expected to become larger at the lower pressure.

Natural attapulgite and sepiolite were heated in two pressure bombs for seven days at 200° C under equilibrium water pressure (about 225 psi) and were found to be stable, at least for that period of time.

Because both magnesium and aluminum constitute the main metal ion components of attapulgite and sepiolite, the stability of the above two natural minerals was examined in the presence of magnesium or aluminum ions. At 200° C under equilibrium water pressure, it was found that attapulgite and sepiolite were stable in magnesium chloride solution in the presence of calcium carbonate and calcium oxide (alkaline medium). Moreover, the attapulgite was examined and compared before and after the $MgCl_2$ treatment. It was observed that attapulgite gave about a 50 percent higher x-ray diffraction intensity (10.5 Å parameter) after $MgCl_2$ treatment than the initial sample. The final aluminum content was the same as initially, but the final magnesium content was found to be higher than the initial content. Therefore, the increase in the x-ray diffraction intensity of the 10.5 Å parameter may be due to the additional formation of octahedral magnesium either in the vacant octahedral layer sites or in the open channels. It was calculated that the additional magnesium was equivalent to about 72 percent of that required to fill all the vacant sites in the octahedral layer.

In aluminum chloride solution containing $CaCO_3$ and CaO (alkaline medium), both attapulgite and sepiolite decompose rapidly into montmorillonite and saponite, respectively, at temperatures lower than 200° C.

It was found that attapulgite in $AlCl_3$ solution containing $CaCO_3$ and CaO starts to decompose into montmorillonite at about 175°C under an equilibrium water pressure. Sepiolite starts to decompose into saponite at about 140°C under an equilibrium water pressure.

Therefore, from the above results it was concluded that attapulgite and sepiolite cannot exist in equilibrium with a solution containing aluminum ions at temperatures above 175°C and 140°C, respectively. Also, the above results suggest that, under the experimental conditions employed, sepiolite is considerably less stable than attapulgite. This conclusion is supported by the acid-dissolution test, where it was found that the rate of decomposition of sepiolite in HCl is about 240 times that of attapulgite. In contrast to this conclusion, McClellan[19] noted that the field relationship in Georgia-Florida deposits where these minerals occur together suggests that sepiolite is more stable to weathering than attapulgite. This observation was based on the vertical decrease upward in attapulgite intensities when a series of samples is examined from stratigraphically superjacent positions.

Free Energy of Formation of Attapulgite and Sepiolite from Solubility Data

Attapulgite

The activity-product constant and the standard free energy of formation of attapulgite were both calculated using the following structural formulas.

1. The ideal structural formula suggested by Bradley

$$(OH_2)_4\ Mg_5Si_8O_{20}(OH)_2\ 4\ H_2O$$

The dissolution reaction can be represented by the following equation.

$$(OH_2)_4Mg_5Si_8O_{20}(OH)_2 \cdot 4\ H_2O + 18\ H_2O = 5\ Mg^{2+} + 8\ H_4SiO_4 + 10\ OH^-$$

Assuming the activities of attapulgite and water are equal to unity, the activity-product constant of the above reaction is represented by

$$K = [Mg^{2+}]^5[H_4SiO_4]^8[OH^-]^{10}$$

$$\log K = 5 \log [Mg^{2+}] + 8 \log [H_4SiO_4] + 10 [OH^-]$$

The concentration results of five different determinations are listed in the following table.

Table 3. Solubility Data for Attapulgite (Attapulgus, Georgia) at Room Temperature

Test No.	Processing Period days	Concentration ppm			pH	pOH
		SiO_2	Mg^{2+}	Al^{3+}		
1	7	92	24.1	0.15	7.7	6.3
2	10	80	15.59	0.15	7.7	6.3
3	14	92	21.9	0.15	7.7	6.3
4	30	84	15.87	0.15	7.8	6.2
5	30	84	16.43	0.15	7.8	6.2
average		86.4	18.78	0.15	7.74	6.26

The activity of H^+ was determined using a glass electrode. H_4SiO_4 was considered to have a unit activity coefficient, while the activity coefficients for Mg^{2+} and $Al(OH)_4^-$ were calculated using the Debye-Hückel equation. The parameters used in this equation are listed by Klotz.[60]

The results are shown below.

Species	Concentration		Activity Coefficient	Activity	-log Activity
	ppm	moles/liter			
SiO_2	86.4	1.44×10^{-3}	1.0	1.44×10^{-3}	2.843
Mg^{2+}	18.78	7.73×10^{-4}	0.887	6.86×10^{-4}	3.164
Al^{3+}	0.15	5.56×10^{-6}	0.975	5.42×10^{-6}	5.266
H^+	---	---	---	---	7.74
OH^-	---	---	---	---	6.26
$Mg^{2+}+1.5Al^{3+}$	---	---	---	6.914×10^{-4}	3.161

If the above solubility data are taken to represent that of the ideal chemical formula, then the standard free energy of formation can be calculated as follows.

Neglecting the activity of $Al(OH)_4^-$, there is obtained

$$\log K = 5(-3.164) + 8(-2.843) + 10(-6.26) = -101.164$$

or

$$K = [Mg^{2+}]^5[H_4SiO_4]^8[OH^-]^{10} = 10^{-101.164}$$

If the activity of $Al(OH)_4^-$ is taken into consideration and the

quantity (Mg^{2+} + 1.5 Al^{3+}) is substituted for (Mg^{2+}), there is then obtained

$$\log K = -101.139$$

and

$$K = 10^{-101.139}$$

Therefore, whether or not the activity of $Al(OH)_4^-$ is considered makes only a very slight difference.

From the Nernst equation

$$\Delta F^\circ_R = -RT \ln K = -1.364 \log K$$

ΔF°_R = 1.364(101.16) = 137.98 kcal/mole, the standard free energy of reaction

The various free energies of formation used in this work are listed in the following table.

Table 4. Standard Free Energies of Formation

Formula	ΔF°_f, kcal	Source
H_2O (liquid)	- 56.69	Rossini, et al. (61)
Mg^{2+}	-108.99	Rossini, et al. (61)
OH^-	- 37.595	Rossini, et al. (61)
$Al(OH)_4^-$	-311.3	Reesman and Keller (38)
H_4SiO_4	-312.65	Reesman and Keller (38)

Using the dissolution equation for attapulgite

$$\Sigma\Delta F^{\circ}_{f} \text{ products} = 5\ \Delta F^{\circ}_{f}\ (Mg^{2+}) + 8\ \Delta F^{\circ}_{f}\ (H_4SiO_4) + 10\ \Delta F^{\circ}_{f}\ (OH^-)$$

$$= 5(-108.99) + 8(-312.65) + 10(-37.595)$$

$$= -3422.1 \text{ kcal}$$

$$\Sigma\Delta F^{\circ}_{f} \text{ reactants} = \Delta F^{\circ}_{f} \text{ attapulgite} + 12\ \Delta F^{\circ}_{f}\ (H_2O)$$

$$= \Delta F^{\circ}_{f} \text{ attapulgite} - 680.28$$

$$\Delta F^{\circ}_{R} = \Sigma\Delta F^{\circ}_{f} \text{ products} - \Sigma\Delta F^{\circ}_{f} \text{ reactants}$$

$$137.98 = -3422.1 - \Delta F^{\circ}_{f} \text{ attapulgite} + 680.28$$

$$\Delta F^{\circ}_{f} \text{ attapulgite} = -2879.8 \text{ kcal/mole, } Mg_5Si_8O_{20}(OH)_2\ 8\ H_2O$$

2. On the average, the attapulgite found in nature has a molar Mg/Al ratio of one. Therefore, the average structure of attapulgite is $Mg_2Al_2Si_8O_{20}(OH)_2\ 8\ H_2O$. According to Reesman and Keller,[38] the species of aluminum ion in solution is controlled by the pH of the solution. At pH values above 6.70, a singly charged anionic species, $Al(OH)_4^-$, was assumed. Therefore, the dissolution equation can be written as follows.

$$Mg_2Al_2Si_8O_{20}(OH)_2\ 8\ H_2O + 12\ H_2O = 2\ Mg^{2+} + 2\ Al(OH)_4^- + 8\ H_4SiO_4 + 2\ OH^-$$

$$K = [Mg^{2+}]^2[Al(OH)_4^-]^2[H_4SiO_4]^8[OH^-]^2$$

$$\log K = 2 \log [Mg^{2+}] + 2 \log [Al(OH)_4^-] + 8 \log [H_4SiO_4] + 2 \log [OH^-]$$

If the solubility data listed in Table 3 are assumed to be representative

for this chemical formula, then the standard free energy of formation can be calculated as follows.

$$- \log K = 2(3.164) + 2(5.266) + 8(2.843) + 2(6.26) = 52.124$$

$$K = 10^{-52.124}$$

$$\Delta F^{\circ}_{R} = 1.364(52.124) = 71.1 \text{ kcal/mole, the standard free energy of reaction}$$

$$\Delta F^{\circ}_{f} \text{ products} = 2\Delta F^{\circ}_{f} (Mg^{2+}) + 2\Delta F^{\circ}_{f} [Al()H)^{-}_{4}] + 8\Delta F^{\circ}_{f} (H_4SiO_4) + 2\Delta F^{\circ}_{f} (OH^{-})$$

$$= 2(-108.99) + 2(-311.3) + 8(-312.65) + 2(-37.595)$$

$$= -3416.97 \text{ kcal}$$

$$\Delta F^{\circ}_{f} \text{ reactants} = \Delta F^{\circ}_{f} \text{ attapulgite} + 12\ \Delta F^{\circ}_{f} (H_2O)$$

$$= \Delta F^{\circ}_{f} \text{ attapulgite} - 680.28$$

$$\Delta F^{\circ}_{R} = \Sigma\Delta F^{\circ}_{f} \text{ products} - \Sigma\Delta F^{\circ}_{f} \text{ reactants}$$

$$71.1 = -3416.97 - \Delta F^{\circ}_{f} \text{ attapulgite} + 680.28$$

$$\Delta F^{\circ}_{f} \text{ attapulgite} = -2807.79 \text{ kcal/mole, } Mg_2Al_2Si_8O_{20}(OH)_2\ 8\ H_2O$$

If the assumption of using the solubility data in Table 3 to represent those of the above two chemical formulas holds true, then it appears that the standard free energy of formation is variable depending on composition. The higher the Mg/Al ratio, the less the number of vacant sites and the more stable the attapulgite is as shown by the larger negative quantity of the standard free energy of formation. This is in accordance with the statement of Bradley[6] that the presence of aluminum weakens the structure of attapulgite.

3. The attapulgite (Attapulgus, Georgia) specimen used in this experiment had the following composition.

Species	Weight (%)
SiO_2	56.00
MgO	12.40
Al_2O_3	7.98
Fe_2O_3	2.51

Therefore, the Mg/Al molar ratio is equal to 1.965, or the number of moles of magnesium is approximately twice that of aluminum. The structural formula for this clay specimen is represented by

$$Mg_{2.86}Al_{1.43}Si_8O_{20}(OH)_2\ 8\ H_2O$$

and the dissolution equation is shown below.

$$Mg_{2.86}Al_{1.43}Si_8O_{20}(OH)_2\ 8\ H_2O + 12\ H_2O = 2.86\ Mg^{2+} + 1.43\ Al(OH)_4^- + 8\ H_4SiO_4 + 4.28\ OH^-$$

$$K = [Mg^{2+}]^{2.86}[Al(OH)_4^-]^{1.43}[H_4SiO_4]^8[OH^-]^{4.28}$$

$$\log K = 2.86 \log [Mg^{2+}] + 1.43 \log [Al(OH)_4^-] + 8 \log [H_4SiO_4] + 4.28 \log [OH^-]$$

$$-\log K = 2.86(3.164) + 1.43(5.266) + 8(2.843) + 4.28(6.26) = 66.144$$

$$K = 10^{-66.144}$$

$\Delta F^\circ_R = 1.364(66.144) = 90.2$ kcal/mole, the standard free energy of reaction

$$\Sigma\Delta F^{\circ}_{f} \text{ products} = -3418.877 \text{ kcal}$$

$$\Sigma\Delta F^{\circ}_{f} \text{ reactants} = \Delta F^{\circ}_{f} \text{ attapulgite} - 680.28$$

$$\Delta F^{\circ}_{R} = \Sigma\Delta F^{\circ}_{f} \text{ products} - \Sigma\Delta F^{\circ}_{f} \text{ reactants}$$

$$90.2 = -3418.877 - \Delta F^{\circ}_{f} \text{ attapulgite} + 680.28$$

ΔF°_{f} attapulgite = -2828.69 kcal/mole, $Mg_{2.86}Al_{1.43}Si_{8}O_{20}(OH)_{2}$ 8 H_2O, the standard free energy of formation

The attapulgite specimen used in this work was found by the acid-dissolution test to contain some impurities. However, the activity-product at equilibrium remains constant regardless of the presence of impurities provided that the attapulgite has control on the activity of one of the products of the dissolution reaction.

The value of the activity-product constant, K, gives an idea of the conditions under which attapulgite may exist. The formation of attapulgite is possible only from solutions where the activity-product of the individual species exceeds that of the activity-product constant.

Sepiolite

Two structural models for sepiolite have been proposed: the Brauner-Preisinger[8] model, $(Si_{12})(Mg_{8})\ O_{30}\ (OH)_{4}\ (OH_2)_{4}$ 8 H_2O, and the Nagy-Bradley[7] model, $(Si_{12})(Mg_{8})\ O_{30}\ (OH)_{6}\ (OH_2)_{4}$ 6 H_2O. The standard free energy of formation was calculated using each of the above structural models for sepiolite.

Two solubility determinations were made and the results are listed in Table 5.

Table 5. Solubility Data for Sepiolite (Asia Minor, Turkey) at Room Temperature

Test No.	Processing Period days	Concentration ppm		pH	pOH
		SiO_2	Mg^{2+}		
6	10	76	1.36	8.0	6.0
7	30	68	0.97	8.2	5.8
average		72	1.165	8.1	5.9

The activities were calculated as for attapulgite. These results are shown below.

Species	Concentration		Activity Coefficient	Activity	-log Activity
	ppm	moles/liter			
SiO_2	72	1.2×10^{-3}	1.0	1.2×10^{-3}	2.921
Mg^{2+}	1.165	4.8×10^{-5}	0.9685	4.64×10^{-5}	4.3335
H^+	--	---	--	---	8.1
OH^-	--	---	--	---	5.9

1. The structural model for sepiolite suggested by Brauner-Preisinger

$$(Si_{12})(Mg_8)\ O_{30}\ (OH)_4\ (OH_2)_4\ 8\ H_2O$$

The dissolution reaction can be represented by the following equation

$$(Si_{12})(Mg_8)\ O_{30}\ (OH)_4\ 12\ H_2O + 18\ H_2O = 8\ Mg^{2+} + 12\ H_4SiO_4 + 16\ OH^-$$

Assuming the activities of sepiolite solid phase and water are unity, the activity-product constant of the above reaction is represented by

$$K = [Mg^{2+}]^{8}[H_4SiO_4]^{12}[OH^-]^{16}$$

$$\log K = 8 \log [Mg^{2+}] + 12 \log [H_4SiO_4] + 16 \log [OH^-]$$

$$-\log K = 8(4.3335) + 12(2.921) + 16(5.9) = 164.12$$

$$K = [Mg^{2+}]^{8}[H_4SiO_4]^{12}[OH^-]^{16} = 10^{-164.12}$$

$\Delta F^\circ_R = 1.364(164.12) = 224$ kcal/mole, the standard free energy of reaction

The values for the standard free energies of formation of the different species of the dissolution reaction are taken from Table 4.

$$\Sigma\Delta F^\circ_f \text{ products} = 8(-108.99) + 12(-312.65) + 16(-37.595) = -5225.24 \text{ kcal}$$

$$\Sigma\Delta F^\circ_f \text{ reactants} = \Delta F^\circ_f \text{ sepiolite} + 18(-56.69) = \Delta F^\circ_f \text{ sepiolite} - 1020.42$$

$$\Delta F^\circ_R = \Sigma\Delta F^\circ_f \text{ products} - \Sigma\Delta F^\circ_f \text{ reactants}$$

$$224 = -5225.24 - \Delta F^\circ_f \text{ sepiolite} + 1020.42$$

$$\Delta F^\circ_f \text{ sepiolite} = -4428.8 \text{ kcal/mole } (Si_{12})(Mg_8)\ O_{30}\ (OH)_4\ 12\ H_2O$$

At the conclusion of this experiment, a similar study by Wollast, Mackenzie, and Bricker[35] was published; however, their approach was different. Equilibrium was approached from the other side of the dissolution equation. They reported the formation of a sepiolite-like product

by adding aqueous silica solution to sea water. The activities of the various species for solutions in equilibrium with the solid product were measured. Then Wollast, et al., calculated the standard free energy of formation of sepiolite to be -4407.0 kcal/mole. This result differs from that reported here by 21.8 kcal/mole or approximately 0.5 percent. Such a difference is quite significant and, therefore, requires explanation.

Wollast, et al. admitted that conventional x-ray diffraction of their precipitates was not satisfactory for determining the nature of the precipitate because the product was too poorly crystallized.

It is to be expected that a highly disorganized product would have a higher solubility than a well crystallized one. This would result in the former having a larger standard free energy of formation and less stability. This is in accord with the general findings of Kittrick[39] and of Reesman and Keller[38] that fire clay has a larger standard free energy of formation than well crystallized kaolinite. Another difference, admittedly very minor, comes from the different free energy values used for aqueous silica. Wollast, et al. have a ΔF°_{f} (SiO_2) of -199.2 kcal/mole taken from Rossini,[61] whereas ΔF°_{f} (H_4SiO_4) of -312.65 kcal/mole as given by Reesman and Keller[38] was employed in the present study. Using the same aqueous silica free energy of formation value would have brought the two standard free energies of formation for sepiolite closer together by 0.84 kcal/mole. Finally, it should be mentioned that the present experiments were made at room temperature which varied between 23°C to 25°C. However, it is likely that the difference in solubility between room temperature and 25°C is negligible for the

purpose of free energy calculations.

The standard free energy of formation of dehydrated sepiolite, $Mg_2Si_3O_8$, can also be calculated. This is equivalent to one fourth of that given by the Brauner-Preisinger formula $(Si_{12})(Mg_8)\ O_{30}\ (OH)_4\ 12\ H_2O$ minus 3.5 moles of H_2O.

$$\Delta F^\circ_f\ (Mg_2Si_3O_8) = 0.25(-4428.8) - 3.5(-56.69) = -908.8 \pm 0.5\ \text{kcal/mole}$$

Wollast, et al. reported $\Delta F^\circ_f\ (Mg_2Si_3O_8) = -903.3 \pm 0.5$ kcal/mole.

2. The structural model for sepiolite suggested by Nagy-Bradley

$$(Si_{12})(Mg_8)\ O_{30}\ (OH)_6\ (OH_2)_4\ 6\ H_2O$$

The dissolution reaction can be represented by the following equation.

$$(Si_{12})(Mg_8)\ O_{30}\ (OH)_6\ 10\ H_2O + 20\ H_2O = 9\ Mg^{2+} + 12\ H_4SiO_4 + 18\ OH^-$$

$$K = [Mg^{2+}]^9[H_4SiO_4]^{12}[OH^-]^{18}$$

$$\log K = 9 \log [Mg^{2+}] + 12 \log [H_4SiO_4] + 18 \log [OH^-]$$

$$-\log K = 9(4.3335) + 12(2.921) + 18(5.9) = 180.25$$

$$K = 10^{-180.25}$$

$\Delta F^\circ_R = 1.364(180.25) = 246.0$ kcal/mole, the standard free energy of reaction

$\Sigma\Delta F^\circ_f$ products $= 9(-108.99) + 12(-312.65) + 18(-37.595) = -5409.43$ kcal

$\Sigma\Delta F^\circ_r$ reactants $= \Delta F^\circ_f$ sepiolite $+ 20(-56.69) = \Delta F^\circ_f$ sepiolite $- 1133.8$

$$\Delta F^\circ_R = \Delta F^\circ_f \text{ products} - \Delta F^\circ_f \text{ reactants}$$

$$246.0 = -5409.43 - \Delta f^{\circ}_{f} \text{ sepiolite} + 1133.8$$

$$\Delta F^{\circ}_{f} \text{ sepiolite} = -4521.6 \text{ kcal/mole, } (Si_{12})(Mg_{8})\ O_{30}\ (OH)_{6}\ 10\ H_2O$$

The sepiolite (Asia Minor, Turkey) specimen used in this determination had the following composition.

Species	Weight (%)	MgO Equivalent
SiO_2	52.0	---
MgO	25.35	25.35
Al_2O_3	0.404	0.483
Fe_2O_3	0.215	0.163
Total		25.996

This gives a molar ratio for SiO_2 to total equivalent MgO of 12 to 8.94, which closely corresponds to that of the Nagy-Bradley formula.

Garrels and Mackenzie[34] determined the solubility product constant for magnesium silicate produced by adding sodium metasilicate to sea water. They represented the formation of sepiolite by the following equation

$$3\ H_2SiO_4 + Mg^{2+} + 2\ OH^- = MgSi_3O_6(OH)_2 + 6\ H_2O$$

They calculated the solubility product constant to be approximately 10^{-24}

$$K = (Mg^{2+})(SiO_2)^3(OH^-)^2 \simeq 10^{-24}$$

The data presented herein give the following results

$$K = (4.64 \times 10^{-5})(1.2 \times 10^{-3})^3(10^{-5.9})^2 = 10^{-24.9}$$

However, it should be mentioned that the chemical formula for sepiolite, $MgSi_3O_8(OH)_2$, as given by Garrels and Mackenzie does not correspond to either the Brauner-Preisinger or the Nagy-Bradley formula.

Kinetics of Acid-Dissolution of Attapulgite and Sepiolite

Partial chemical analyses for air dried attapulgite and sepiolite are given in the following table.

Table 6. Partial Chemical Analyses of Attapulgite and Sepiolite

Percent	Attapulgite	Sepiolite
SiO_2	56.00	52.00
MgO	12.40	25.350
Al_2O_3	7.98	0.404
Fe_2O_3	2.51	0.215

The hydrochloric acid employed for dissolution was equivalent to about 85 times the amount needed for complete reaction with the Mg, Al, and Fe in attapulgite; for sepiolite it was about 19 times the amount required to react with the Mg. Therefore, the HCl concentration remained virtually constant during the reaction. When the digestion times were relatively short, the residual cations were calculated indirectly by subtracting the percent soluble from the total percent in the sample.

For longer digestion times, the residue was analyzed directly. Acid-dissolution curves were obtained by plotting the residual cations, expressed as the oxide, versus time on semilogarithmic paper. By definition, a straight-line relationship represents a first-order reaction with respect to the cations, Mg, Al, and Fe. This is based on the assumption that the volume of the clay remains constant during the reaction. The assumption seems to be reasonable, as the molecular structure does not collapse until most of the metal ions are extracted.

Data on the acid-dissolution of attapulgite were obtained at temperatures of 60.0, 70.3, 80.1, and 91.2°C using 5.0 N HCl. The data are listed in Tables 11-14 in Appendix C and are plotted in Figures 4-7.

The figures show that the curves for Mg, Al, and Fe have high slopes upon initiation of the reaction, then level off becoming straight lines. The straight line portions for the Mg must represent the octahedral ion, since Mg does not occur in the tetrahedral layer. By analogy, the straight line portions for the Al and Fe curves represent octahedral Al and Fe.

The first part of the curves for Mg, Al, and Fe represents extraneous material which produces the high reaction rate and which is completely reacted in a short time. Extrapolation of the straight line portion of the curves indicates the early soluble material amounts to approximately four percent MgO, two percent Al_2O_3, and one percent Fe_2O_3. A small portion of this material is present as exchange material, but most of it must occur on the clay surface or in the attapulgite channels.

Approximately one third of the cations that normally are assumed to be in the octahedral layer are apparently present as impurities.

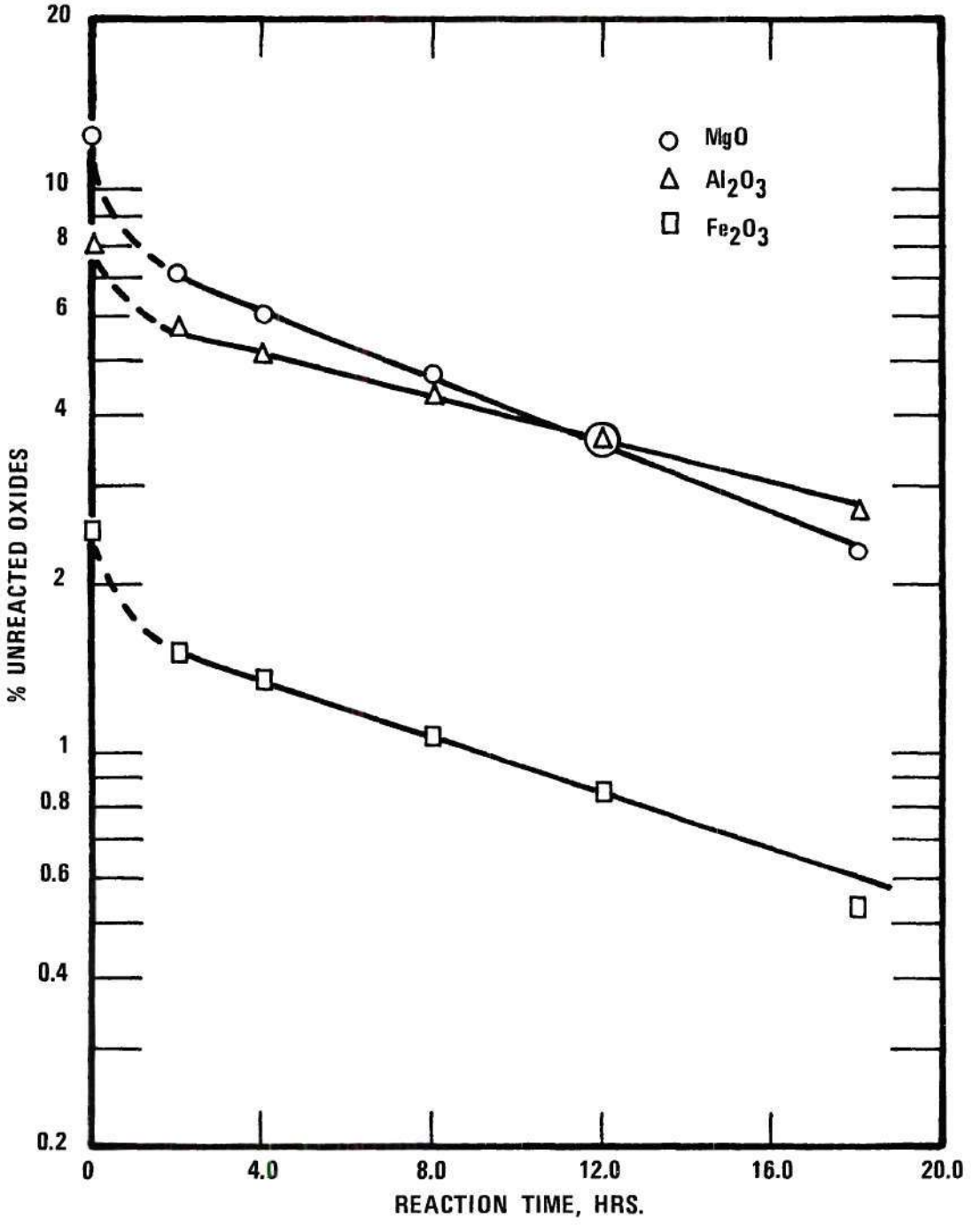

Figure 4. Reaction Rate of Attapulgite (Attapulgus, Georgia) with 5.0 N HCl at 60° C

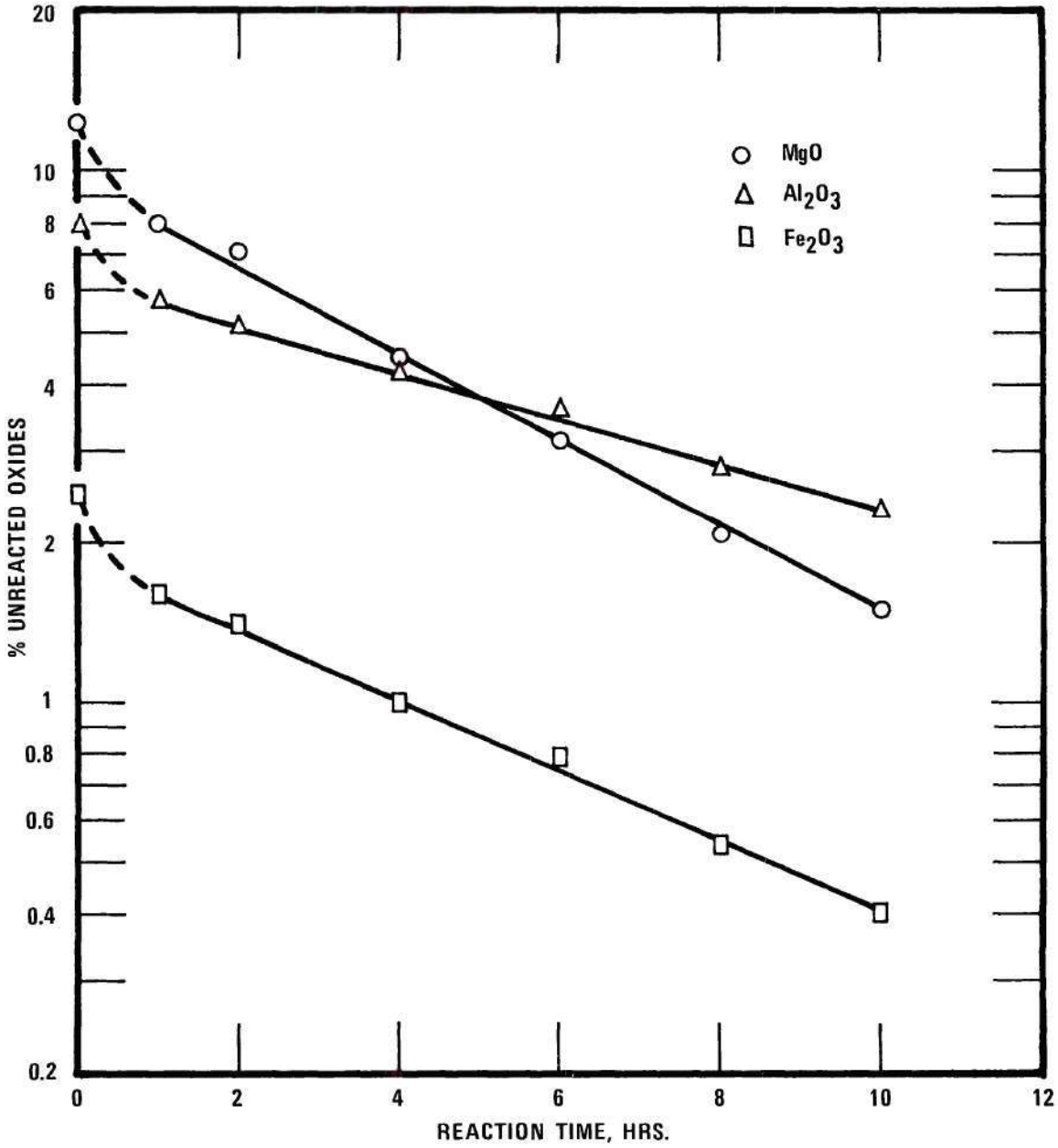

Figure 5. Reaction Rate of Attapulgite (Attapulgus, Georgia) with 5.0 N HCl at 70.3°C

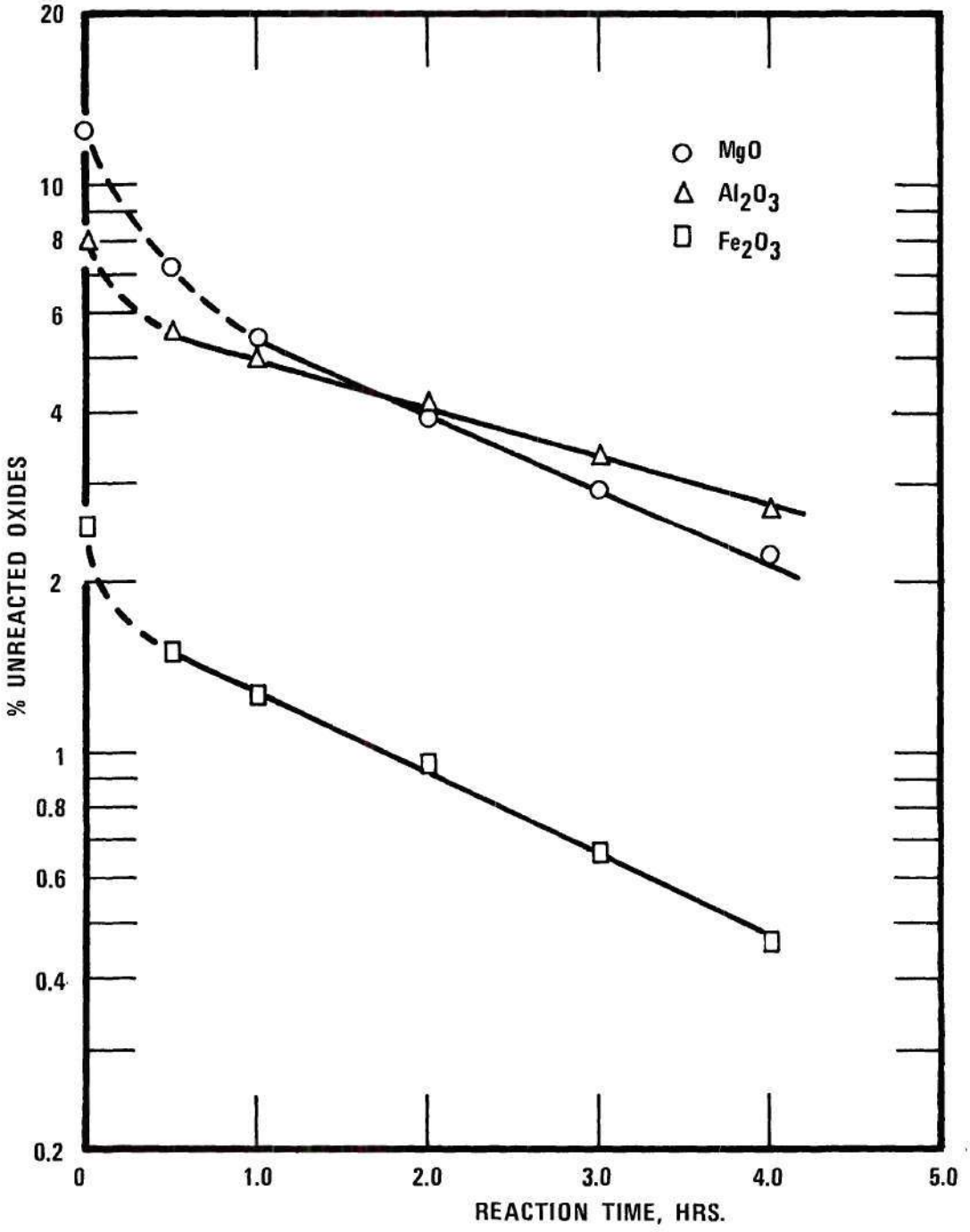

Figure 6. Reaction Rate of Attapulgite (Attapulgus, Georgia) with 5.0 N HCl at 80.1°C

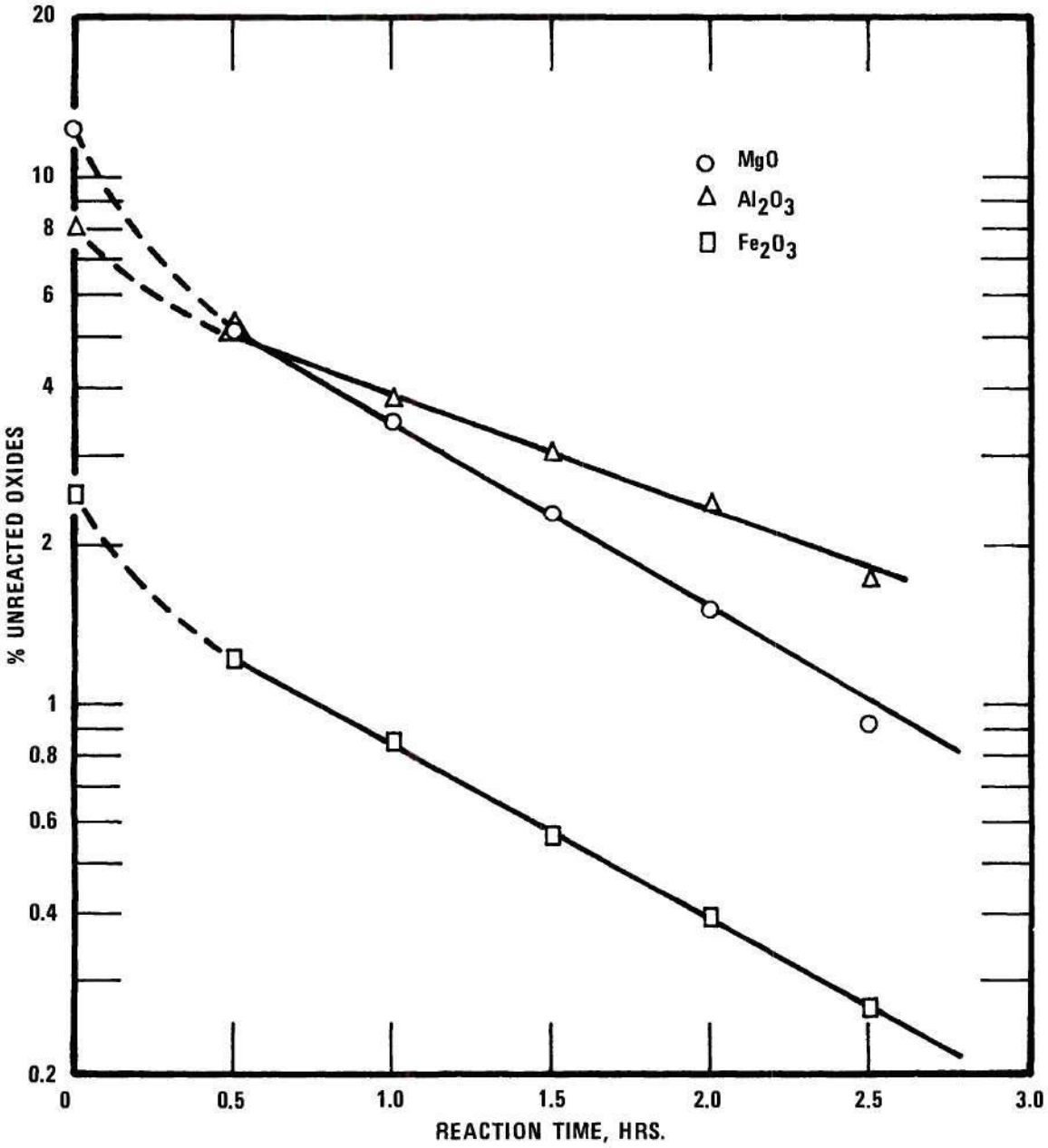

Figure 7. Reaction Rate of Attapulgite (Attapulgus, Georgia) with 5.0 N HCl at 91.2° C

This indicates that fewer of the five octahedral positions are filled than the four suggested by Bradley.[6] Calculations based on the original analysis (assuming 21 oxygens) indicate that 4.16 octahedral positions are filled. Calculations based on the extrapolated data obtained from the 60°C curves (6.10 percent Al_2O_3, 1.7 percent Fe_2O_3, 8.10 percent MgO) indicate 3.18 of the possible 5.00 octahedral positions are filled. The calculations also indicate excess Si is present; however, it is unlikely that the Si excess is sufficient to cause a major increase in the calculated octahedral cation population. The SiO_2 value would have to be lowered to approximately 45 percent to allow for a calculated value of 4.0 filled octahedral positions. Approximately two octahedral positions are filled with the large Mg and Fe ions and one by the small Al ion. On the basis of the dissolution data and the strain induced by the difference in cation size, it could be speculated that the Mg and Fe ions fill the two edge positions and the Al ion the center position, with the two intermediate positions being vacant. Charge deficiencies would be made up by H ions.

This is in accordance with Bradley,[6] who said that the distribution of Al ions among the five available octahedral positions in a chain can be accommodated either by vacancies in the octahedral positions or by some replacement of Si by Al. The former seems more likely for the present sample. When larger percentages of Al and Fe than shown in the graphs were dissolved, the attapulgite structure collapsed and the assumption of constant volume for the clay during the reaction became invalid. This break-up of the attapulgite is reflected by an increase in the slopes of the dissolution curves. As the slopes for the tetrahedral

cations are lower than their corresponding octahedral cations, as reported by Brindley and Youell[41] and by Osthaus,[42] no evidence was obtained to suggest the presence of tetrahedral Al and Fe.

The results of Osthaus[42,43] for montmorillonite and nontronite indicate approximately equal reaction rate constants for Mg, Al, and Fe. The slopes of the curves in Figures 4-7 show that Mg and Fe have a higher reaction rate constant than Al. An explanation, as suggested previously, would be that the Al is concentrated in the interior positions and the Mg and Fe in the edge positions.

Attapulgite was also digested with 2.5 N HCl at 70.3°C. The results are listed in Table 15 (Appendix C). The dissolution data for attapulgite with 2.5 N and 5.0 N HCl are plotted in Figures 8 and 9. For the corresponding cations, the slopes of the curves for 5.0 N HCl are about twice those for 2.5 N HCl. Therefore, the reaction is also of first order with respect to acid concentration. This result is similar to that found by Osthaus[42,43] for montmorillonite and nontronite and by Gastuche[45] for biotite.

The first-order, rate equation states that the reaction rate is proportional to the concentration of the reactants as shown below

$$\frac{dM}{dt} = -kM \qquad (1)$$

where M is the concentration of undissolved metal ion, t the time, and k the apparent rate constant.

Integrating equation (1) between the limits of time t_1 and t_2 for the straight line portion of the curve yields

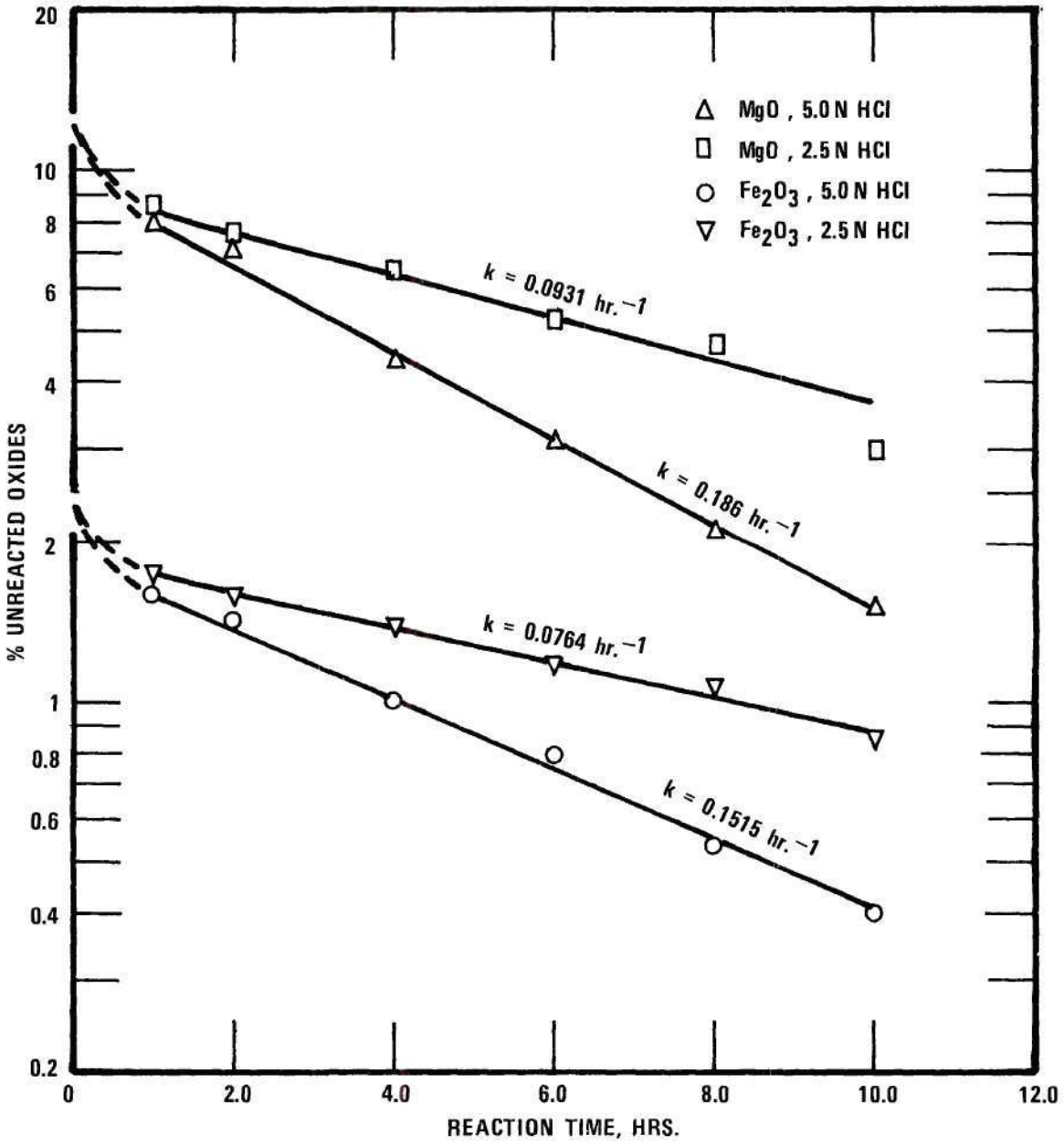

Figure 8. Reaction Rate of Attapulgite (Attapulgus, Georgia) with HCl at 70.3°C

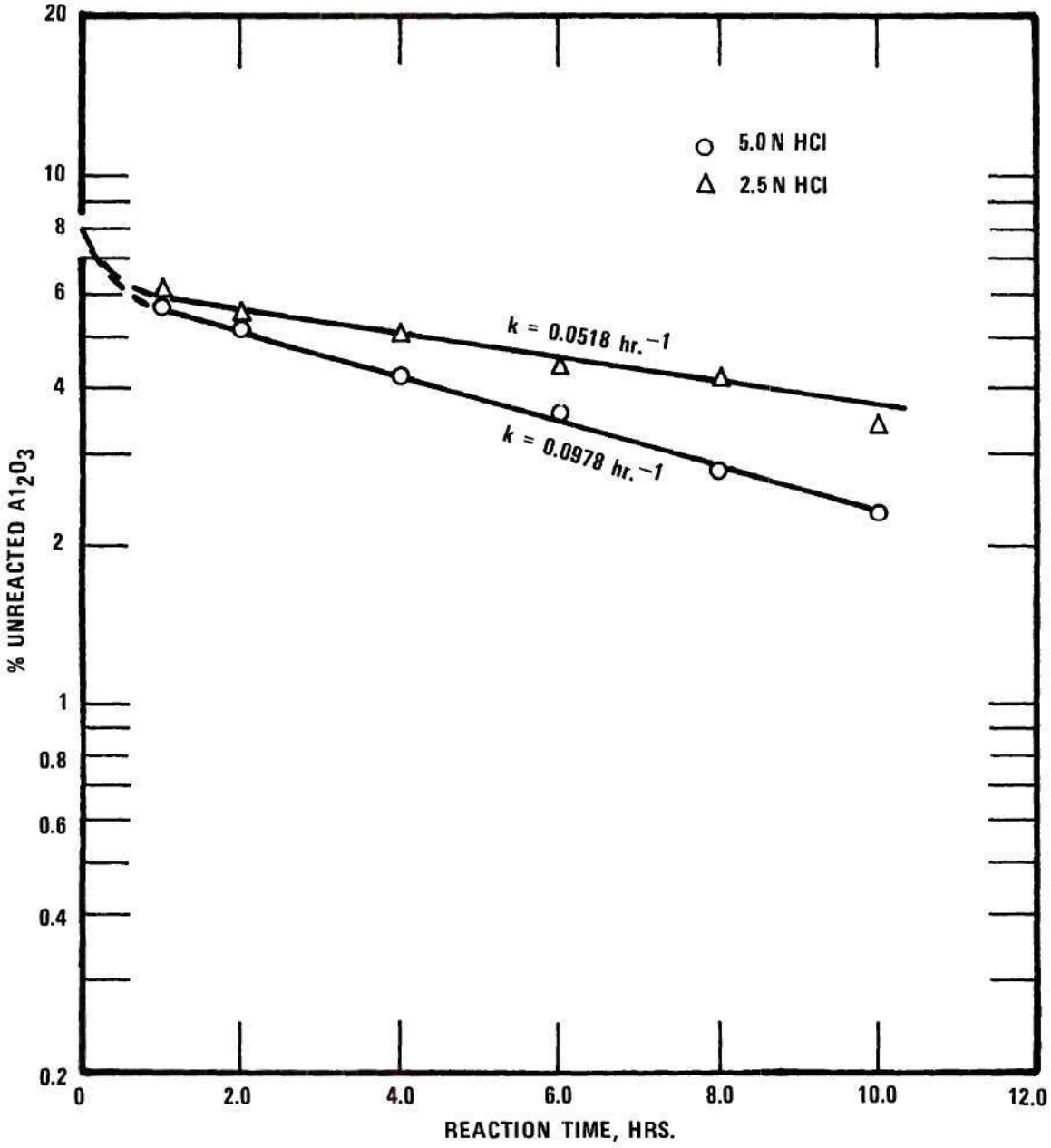

Figure 9. Reaction Rate of the Al_2O_3 Component of Attapulgite (Attapulgus, Georgia) with HCl at 70.3° C

$$\ln \frac{M_1}{M_2} = k(t_2 - t_1) \qquad (2)$$

Using common logarithms, the equation becomes

$$\log \frac{M_1}{M_2} = \frac{k(t_2 - t_1)}{2.3} \qquad (3)$$

Therefore, the apparent rate constant as defined by Osthaus[43] is 2.3 times the slope of the straight line in the semilogarithmic plot. Table 7 lists the apparent rate constants of attapulgite with 2.5 N and 5.0 N HCl at 70.3°C.

Table 7. Apparent Rate Constants of Octahedral Mg, Al, and Fe in Attapulgite with HCl at 70.3°C

HCl Concentration	Apparent Rate Constant k, hr^{-1}		
	Mg	Al	Fe
2.5 N	0.0931	0.0518	0.0764
5.0 N	0.186	0.0978	0.1515

As the reaction is also of first order with respect to acid concentration, equation (1) can be rewritten to give account of the acid concentration as shown below

$$\frac{dM}{dt} = -k^* A M \qquad (4)$$

where A is the acid concentration and k* is the true rate constant, which is independent of acid concentration.

Integrating equation (4) considering A constant gives

$$\ln \frac{M_1}{M_2} = k^* A (t_2 - t_1) \qquad (5)$$

Comparing equations (2) and (5), there is obtained

$$k = k^* A \qquad (6)$$

Therefore, the true rate constant k* is calculated by dividing the apparent rate constant k by the acid concentration A in moles per liter. The true rate constants for the octahedral cations in attapulgite are calculated at the four different temperatures employed and are listed in the following table.

Table 8. True Rate Constants with HCl of Octahedral Mg, Al, and Fe in Attapulgite

Temperature °C	1000/T†	True Rate Constants, k*		
		Mg	Al	Fe
60	3.002	0.01412	0.00882	0.01156
70.3	2.9115	0.0372	0.01956	0.0303
80.1	2.831	0.0614	0.0398	0.0539
91.2	2.7445	0.1666	0.1016	0.1502

†T is the absolute temperature in degrees Kelvin.

From the Arrhenius equation

$$k = A\, e^{-E/RT} \tag{7}$$

where k is the rate constant, hr^{-1}, A is a constant, E is the activation energy in calories per mole, R is the gas constant in calories per degree per mole, and T is the absolute temperature in degrees Kelvin.

The logarithmic expression of equation (7) is

$$\log k = -E/2.303\ RT + C \tag{8}$$

Therefore, a plot of the rate constant versus the reciprocal of the absolute temperature on a semilogarithmic paper gives a straight line with a slope equal to -E/2.303 R.

A plot of the true rate constants for the octahedral cations in attapulgite versus the reciprocal of the absolute temperature is shown in Figure 10. This figure shows that the three straight lines for Mg, Al, and Fe are approximately parallel indicating equal activation energies for the above cations. The activation energy was calculated to be 18.4 kilocalories per mole. This value is essentially in the same range as that found by Osthaus[43] for montmorillonite and nontronite (17-18 kilocalories per mole).

The acid-dissolution data for sepiolite (Asia Minor), obtained at 30.5°C for 1.0 N HCl, are listed in Table 16 (Appendix C).

A semilogarithmic plot of the residual magnesium oxide versus time is shown in Figure 11. Unlike attapulgite, the curve for sepiolite is a straight line which passes through the origin. This indicates that

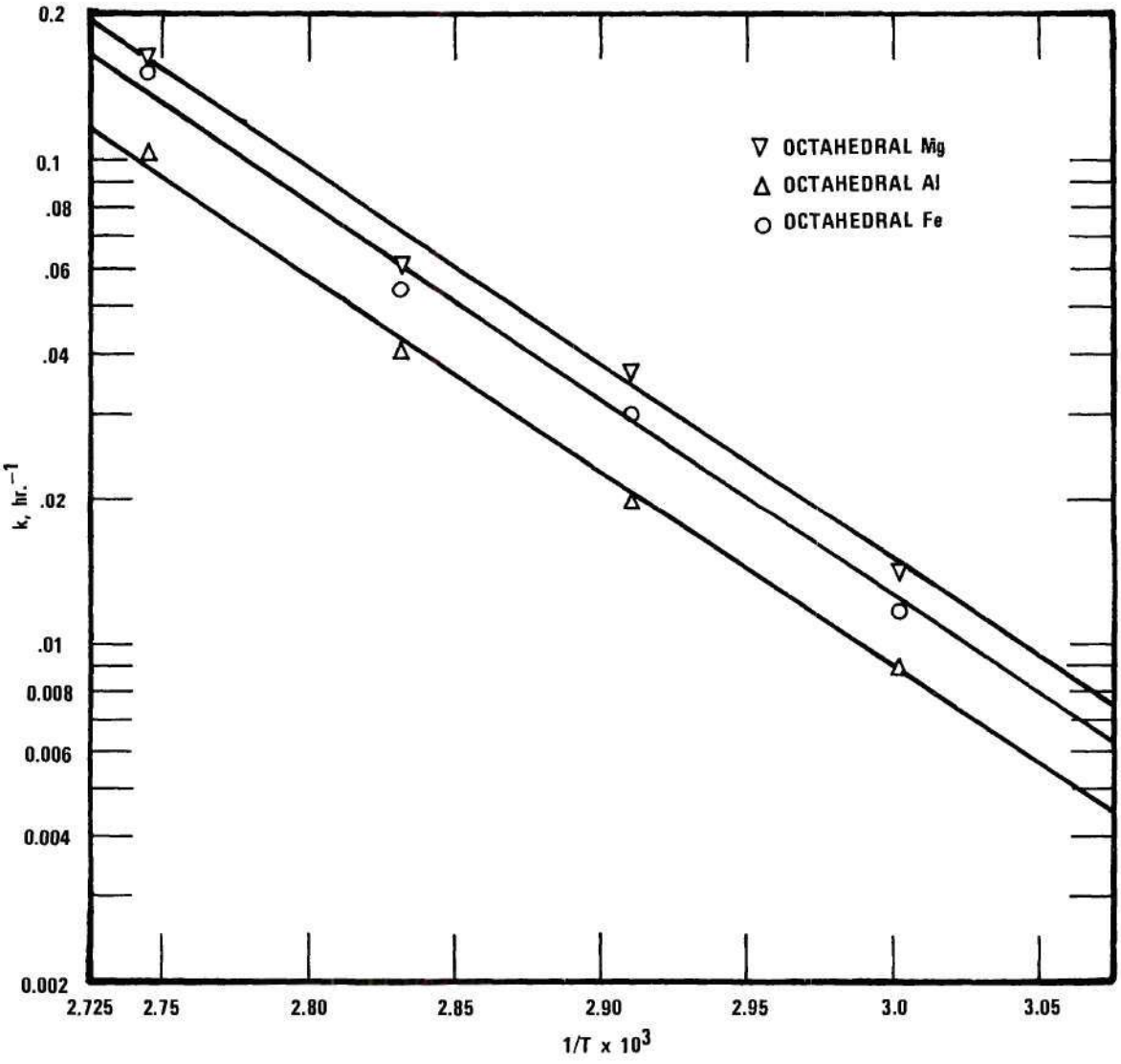

Figure 10. Rate Constant in HCl of Octahedral Mg, Al, and Fe in Attapulgite (Attapulgus, Georgia) versus the Reciprocal of the Absolute Temperature

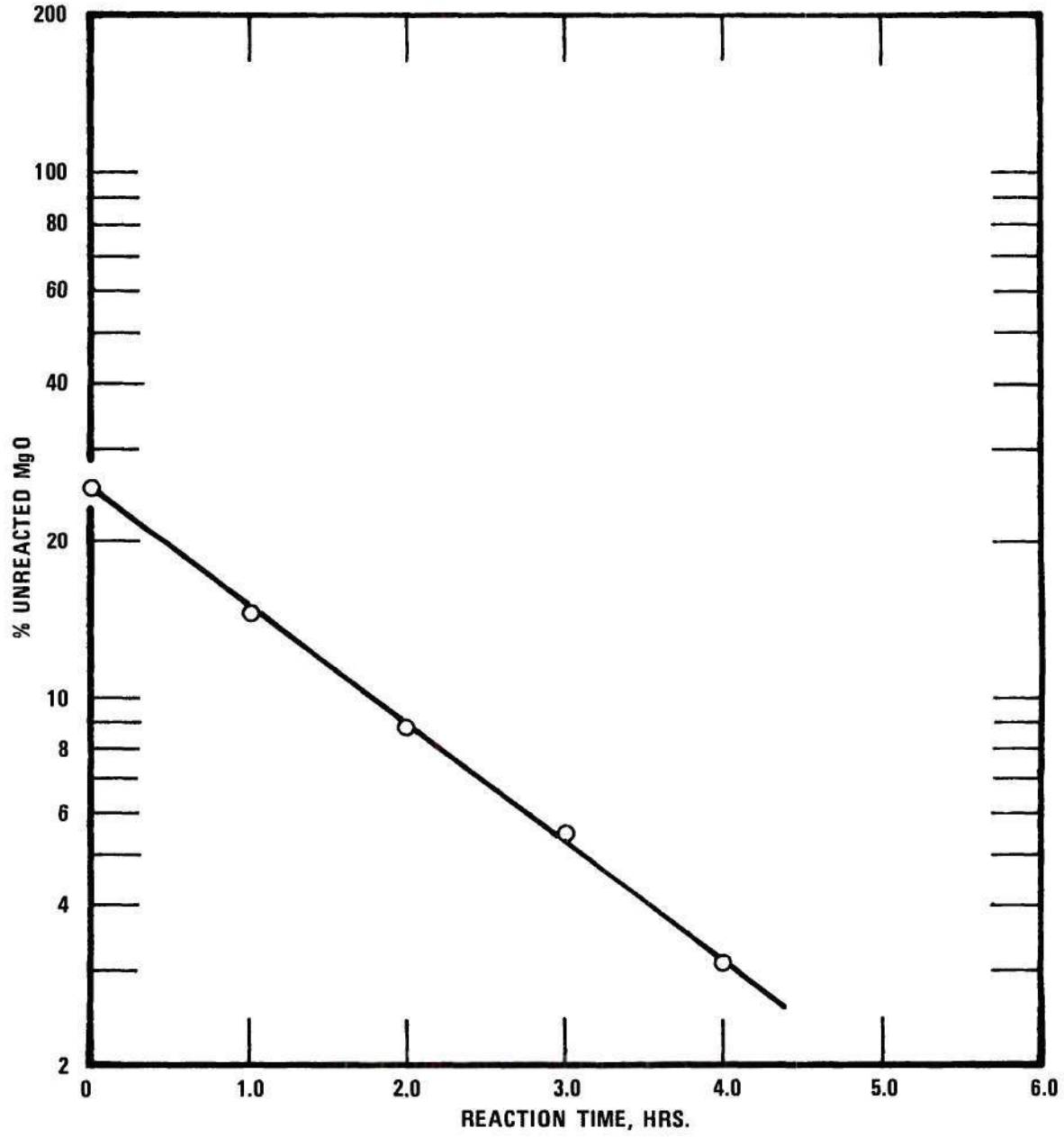

Figure 11. Reaction Rate of Sepiolite (Asia Minor, Turkey) with 1.0 N HCl at 30.5° C

all the magnesium ions are in the octahedral layer. The true rate constant at 30.5° C was calculated to be 0.553 per hour. Compared to attapulgite, the rate constant for sepiolite is larger by a factor of about 240. This indicates that sepiolite is less stable to acid weathering than attapulgite.

Model for Attapulgite and Sepiolite Reactions

Osthaus[43] suggested that the acid-dissolution of a completely expandable mineral can be considered as essentially analogous to a liquid-liquid reaction. In the case of montmorillonite and nontronite, he suggested that the metal ions can migrate through the edges and particularly the surfaces of the clay platelets and that the solid-liquid boundary has little or no differential effect on the transfer of ions. Osthaus suggested that if the clays are not expandable or only partially expandable, the transfer of metal ions may take place only at the edges of the platelets in which case the migration of ions would be affected by the rate of diffusion through the crystal structure.

As attapulgite and sepiolite are not expandable, a mechanism different from that for montmorillonite and nontronite must be operative.

The continuous reaction model may apply. It is assumed that the reactant fluid enters and reacts throughout the solid particle at all times, most likely with different rates at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle. This model is reported by Levenspiel[62] to be the most reasonable representation of the actual phenomenon for the slow reaction of a very porous solid. The above requirements

for the continuous reaction model seem to be satisfied for the acid-dissolution of attapulgite and sepiolite, as both minerals are highly porous due to the presence of open channels and the reaction is relatively slow at moderate temperatures.

Walker, Rusinko, and Austin,[63] drawing on the ideas relating to catalytic gas-solid reactions, have used the continuous-reaction model to develop in detail the kinetic equations for heterogeneous noncatalytic reaction. They have applied this model to the gas-carbon system.

Heterogeneous reaction rates involving a porous solid and a fluid may be controlled by one or more of the following steps:

1. mass transport of the reacting fluid from the exterior solid surface across a relatively stagnant fluid film between the exterior solid surface and the main fluid stream;

2. because the interior of the particle contains much more area than the exterior, most of the reaction takes place within the particle itself; therefore, this step comprises the mass transport of the reacting fluid from the exterior surface of the solid to an active site beneath the surface and mass transport of the products in the opposite direction;

3. chemisorption of reactant, wholly or in part; a rearrangement of chemisorbed species on the surface to a desorbable product; and desorption of the product from the surface.

Walker, et al.[63] considered three temperature zones. The low temperature zone is one in which the reaction rate is controlled solely by the chemical reactivity of the solid (step 3). The measured or apparent activation energy is equal to the true activation energy. In

this zone the concentration gradient of the reacting fluid is quite small. In the intermediate temperature zone, the concentration of the reacting fluid approaches zero at a distance from the exterior surface less than the radius of the particle. The reaction rate is controlled jointly by steps 2 and 3. It was shown that the apparent activation energy is one half of the true activation energy in this zone. It seems that the activation energies for bentonite and biotite calculated by Granquist and Sumner[44] and by Gastuche[45] were within this temperature zone, since their results are rather low. In the high temperature zone, the concentration of the reactant species approaches a small value at the exterior surface of the solid and the reaction rate is controlled by step 1.

The temperature range used in the clay-acid reaction (30°-90° C) is moderate and it is believed that this range lies within the low temperature zone where surface phenomenon is controlling (step 3). Evidence for this is that the reaction rate constant was found to vary exponentially with temperature. For this condition, Levenspiel[62] reported that the experimental data for irreversible reaction could usually be represented by a first-order rate equation, n^{th} order rate equation, or similar equations when more than one reactant was involved.

Reversibility of the Clay-Acid Reaction

Mering[64] studied the activation of montmorillonites by treating them with hot concentrated acids. He found that, when the octahedral ions had been largely removed and an amorphous product formed, it was possible to reconstitute a montmorillonite-type product by treating the residue with a solution containing magnesium ions. He deduced that the

Si-O network was not fully destroyed when the octahedral ions had been extracted.

Brindley and Youell,[41] likewise, found that it was possible to reconstitute the Si-(Al)-O networks from a chlorite into the mica-like product with a characteristic 10 Å spacing.

In this work, the reconstitution of attapulgite was examined. Each of the residues of the attapulgite digested with 5.0 N HCl at 70.3° C was divided into two portions. One portion was treated with very dilute sodium hydroxide solution (pH = 9). The mixture was placed in a stainless steel pressure bomb, which was heated in the oven at 110° C for two days. The other portion was treated under similar conditions with magnesium chloride solution containing 1000 ppm Mg. The pH was also adjusted to nine with sodium hydroxide. It was noticed that there was a small decrease in pH in the first case, while in the second case the decrease in pH was quite appreciable. The x-ray intensities of the 10.5 Å spacing for the treated samples were compared with those of the initial residue. The results are shown in Table 9.

It is believed that the increase in the x-ray intensity of the 10.5 Å spacing after the NaOH treatment is mainly due to the dissolution of amorphous silica which was formed during the attapulgite acid reaction. The sodium ions are too large to enter in the octahedral layer and occupy a vacant site. However, the large increase in the x-ray intensity of the 10.5 Å spacing after the $MgCl_2$ treatment could be interpreted to indicate that there was some reconstitution and some Mg had entered the octahedral layer. In the acid dissolution, the Mg, Al, and Fe ions in the octahedral layer are supposed to be displaced by H

Table 9. Reconstitution Data

Time of treatment of attapulgite with 5.0 N HCl at 70° C, hours	X-ray intensity, 10.5 Å (0.1 inch units)			pH, NaOH Treatment		pH, $MgCl_2$ Treatment	
	Initial Residue	After NaOH Treatment	After $MgCl_2$ Treatment	Initial	Final	Initial	Final
2	35	50	69	9.3	8.5	9.0	6.2
4	15	28	47	9.2	8.9	9.0	6.2
8	13.5	18	36	9.2	8.6	9.0	6.1
10	9	14.5	20	9.0	8.4	9.0	6.2

ions. If Mg ions are able to enter the octahedral layer and displace the H ions, an appreciable decrease in the pH of the solution would occur. That this has occurred is shown by the pH data in Table 9.

In another experiment, the original attapulgite was treated with $MgCl_2$ solution under the same conditions as above. It was found that the x-ray intensity of the 10.5 Å increased from 50 to 90 (0.1 inch) after the $MgCl_2$ treatment. The residue was analyzed and found to contain a higher ratio of Mg than did the original sample. Only H ions were found in the reacting fluid. The initial pH was 9.4 and the final pH 7.5. It was calculated that the increase in Mg was equal to about 72 percent of that needed to fill completely the vacant sites in the octahedral layer. It seems quite likely that the Mg entered the octahedral layer.

The reconstitution of attapulgite is possible up to about 90 percent dissolution of the octahedral cations. A skeleton framework must exist up to this point. Complete dissolution of the octahedral cations resulted in destruction of the structure. The product was amorphous to x-ray, and it was not possible to reconstitute the material to attapulgite by treating it with $MgCl_2$.

Origin of Attapulgite and Sepiolite

Some of the hypotheses on the origin of attapulgite and sepiolite are examined below.

1. Kerr[9] suggested that attapulgite from Georgia was formed by the alteration of montmorillonite minerals. Reynolds[10] believed that both attapulgite and sepiolite from Florida were formed by the alteration of montmorillonite. Bonatti and Joensuu[11] suggested that attapul-

gite in deep sea sediment was formed by the hydrothermal alteration of montmorillonite by the action of Mg-rich solutions. Parry and Reeves[12] believed that the sepiolite found in Mound Lake was formed from montmorillonite as a result of exposure to alkaline lake brine rich in magnesium. Heystek and Schmidt[13] suggested that attapulgite in the Springbok Flats, Transvaal, was formed from the weathering of basalt with montmorillonite as the intermediate weathering product. Loughnan[14] proposed that attapulgite and sepiolite in the Redbank Plains, Queensland, Australia, were formed by the reaction of weathered basalt with magnesium rich water, with montmorillonite as an intermediate.

All of the above hypotheses can be summed up by the following equation.

$$\text{montmorillonite} + Mg^{2+} \xrightarrow{\text{alkaline pH}} \text{attapulgite and/or sepiolite}$$

This equation was examined by performing the following experiments.

(a) A mixture of montmorillonite and $MgCl_2$ solution containing 1000 ppm Mg was prepared, the pH was adjusted to 9.4 with NaOH, the mixture was placed in a stainless steel pressure bomb and heated at 110°C under equilibrium water pressure for various periods of time up to 21 days.

(b) The same mixture as in (a) was adjusted to a pH of 9.4 with CaO and heated at 150°C for seven days.

(c) The same mixture as in (a) was adjusted to a pH of 8.5 with $CaCO_3$ and heated at 200°C for up to 10 days.

(d) The same mixture as in (c), except that dolomite was em-

ployed as the source of Mg^{2+}. The slurry was heated at 200°C under equilibrium water pressure for up to 16 days.

(e) The same mixture as in (c), except that sepiolite was used as the source of Mg^{2+}. The pH of the slurry was made alkaline with $CaCO_3$ and it was heated at 200°C under equilibrium water pressure for up to 10 days.

None of the above experiments resulted in the alteration of montmorillonite into attapulgite and/or sepiolite. Because montmorillonite is more stable than either attapulgite or sepiolite, it would appear highly unlikely that it would convert into attapulgite or sepiolite under the conditions of the above experiments.

2. Longchambon[17] suggested that attapulgite was derived from sepiolite by the isomorphous substitution of magnesium by aluminum. This can be represented by the following equation.

$$\text{sepiolite} + Al^{3+} \longrightarrow \text{attapulgite} + Mg^{2+}$$

A mixture of sepiolite and $AlCl_3$ solution containing 200 ppm Al was prepared. The slurry was rendered slightly alkaline with $CaCO_3$ and CaO, and the slurry was heated in a pressure bomb at various temperatures under equilibrium water pressure. It was found that at approximately 140°C and above, sepiolite converted into saponite rather than attapulgite. Below 140°C no change was observed. Therefore, no experimental proof of this hypothesis could be obtained.

3. Loughnan[14] suggested the following transformation sequence for the reaction of weathered basalt with magnesium rich water.

montmorillonite $\xrightarrow{Mg}$ attapulgite $\xrightarrow{Mg}$ sepiolite $\xrightarrow{Mg}$ dolomite

A mixture of attapulgite and $MgCl_2$ solution was prepared. The slurry was made alkaline with $CaCO_3$ and CaO. Heating this mixture at various temperatures up to 200° C under equilibrium water pressure did not convert the attapulgite into sepiolite. On the contrary, the x-ray intensity of the 10.5 Å spacing was found to increase after heating, suggesting an increase in the crystallinity of attapulgite.

4. Demangeon and Salvayre[49] believed that attapulgite in duMont-Perdu, Spain, was formed from magnesium (derived from dolomite), silica (derived from quartz), and aluminum (derived from other clay minerals).

Two mixtures of dolomite, silica, and $AlCl_3$ solution were heated at 200° C under equilibrium water pressure for three days. Only saponite was identified in the product. The x-ray diffraction intensity of the 17 Å spacing was found to increase with an increase in aluminum content of the initial mixture. In another experiment, montmorillonite was employed instead of $AlCl_3$ as the source of aluminum. No change was observed after heating the mixture.

5. Millot, Lucas, and Wey[51] suggested that montmorillonite, attapulgite, and sepiolite in North Africa was formed by the reaction of silica tetrahedrons with such ions as Al and Mg in an alkaline environment. He termed the process "neoformation."

Mixtures containing $MgCl_2$, $AlCl_3$, and SiO_2 were reacted at temperatures varying from room temperature to 200° C. The only crystalline phase obtained was montmorillonite or saponite. Neither attapulgite nor sepiolite could be detected by x-ray diffraction.

6. Lapparent[18] suggested that sepiolite is formed by the action of magnesium-rich solutions upon siliceous gels in the presence of lime. Shabayeva[50] believed that attapulgite from Southeastern Turkmenia was produced in a weakly alkaline medium by the reaction of magnesium ions and silica released by the decomposition of volcanic ash. Rogers, Martin, and Norrish[15] proposed that tropical weathering of basalt in Queensland, Australia, released alkali, alkaline earth metals, and silicon. Calcium, magnesium, and silicon from the basalt appear to have accumulated in lakes and precipitated out as dolomite, sepiolite, and chert. McClellan[19] postulated that attapulgite in the Florida-Georgia region was formed by the action of high magnesium sulfate spring solutions on siliceous sediments which consisted of siliceous diatom valves and possibly detrital clay materials. The carbonates associated with the attapulgite protected the attapulgite from acid groundwater attack.

The above hypotheses can be represented by the equation below.

$$Mg^{2+} + SiO_2 \xrightarrow{\text{alkaline pH}} \text{attapulgite or sepiolite}$$

Mixtures of $MgCl_2$ or $MgSO_4$ solutions and various forms of silica, including amorphous silica and opal-cristobalite, were reacted in alkaline media at temperatures between room temperature and 200°C under equilibrium water pressure. At the lower temperatures, the montmorillonoid group was produced, whereas, at higher temperatures, serpentine was formed. Neither attapulgite nor sepiolite could be detected by x-ray diffraction in the reaction product.

CHAPTER V

CONCLUSIONS

From the results of this investigation, the following conclusions are obtained.

1. In the system $MgO-SiO_2-H_2O$ over the temperature range from 25° to 200°C, lower temperatures favor the formation of 2:1 layer silicates, while higher temperatures favor the formation of 1:1 layer silicates.

2. In magnesium-aluminum double hydroxide systems with low Mg/Al ratio, the formation of montmorillonite is favored while the formation of saponite is favored by high Mg/Al ratios. In the intermediate range, serpentine minerals are formed. Pure $Al(OH)_3$ forms boehmite, while pure $Mg(OH)_2$ forms serpentine minerals. These serpentine minerals have slightly different spacings, depending on the Mg/Al ratio of the reactant. The larger this ratio the larger the spacing.

3. Some of the reaction products in the clay synthesis experiments contain fibrous shaped materials. However, attapulgite or sepiolite could not be positively identified by x-ray diffraction.

4. In solutions containing aluminum ions under alkaline conditions, attapulgite decomposes at about 175°C under equilibrium water pressure, while sepiolite decomposes at about 140°C. Therefore, under these conditions attapulgite has a wider field of stability than sepiolite.

5. The standard free energy of formation of attapulgite and sepiolite was determined from aqueous solubility data. The standard free energy of formation for dehydrated sepiolite, $Mg_2Si_3O_8$, was found to be -908.8 ± 0.5 kcal/mole. For attapulgite, ΔF°_f was found to be -2828.7 kcal/mole of $Mg_{2.86}Al_{1.43}Si_8O_{20}(OH)_2\ 8\ H_2O$.

6. In the acid-dissolution of attapulgite and sepiolite, the reaction is found to be of first order with respect to the metal ion concentration in the residue and also with respect to the acid concentration.

7. The reaction rate constants for octahedral Mg, Al, and Fe in attapulgite are found to be unequal. Magnesium has the largest, iron the intermediate, and aluminum the lowest rate constant. One explanation is that Al is concentrated in the interior position of the octahedral structure, while Mg and Fe are concentrated in the edge positions.

8. The reaction rate constant of Mg in sepiolite is found to be about 240 times larger than in attapulgite. Sepiolite seems to be less resistant to acid weathering than attapulgite.

9. No evidence was obtained to indicate the presence of either tetrahedral Al or Fe in attapulgite.

10. The activation energy of acid-dissolution for each of the octahedral Mg, Al, and Fe ions is the same and equal to about 18.4 kcal/mole.

11. Treatment of partially acid-digested attapulgite with Mg ions under alkaline conditions results in an increase in the x-ray intensity of the 10.5 Å spacing, suggesting that some of the attapulgite is reconstituted.

12. Some of the hypotheses of the origin of attapulgite and sepiolite were checked. However, under the experimental conditions used, none of them proved to be satisfactory.

CHAPTER VI

RECOMMENDATIONS

The following are recommended for consideration in future investigations of this type.

1. Determine the kinetics of acid dissolution of sepiolite at various temperatures. From these data, calculate the activation energy of acid dissolution for sepiolite.

2. Since many of the synthetic products are practically amorphous to x-ray, additional methods for examining the reaction products are needed; infrared spectroscopy, electron diffraction, and differential thermal analysis are suggested. In addition, a transmission Laue camera is needed in order to obtain the more sensitive x-ray data for powders.

3. Calculate the free energy of formation of natural attapulgite and sepiolite at several temperatures. Then find the temperature at which the free energy of formation is least. This temperature will be the optimum for the formation of synthetic attapulgite and sepiolite. At temperatures other than 25° C, the free energy of formation can be calculated by following the method of Hostetler, et al.[40] for serpentine.

4. Solutions of concentration slightly above the solubility of the mineral needed to be synthesized must be used. At this condition, the reaction is reversible and, therefore, more of the mineral will be formed in order to shift the solution concentration back to the satura-

tion level. The solution concentration should occasionally be adjusted to the initial concentration. Also, the pH should be adjusted to that of a solution in equilibrium with the natural mineral. The addition of a few crystals of the natural mineral would be helpful.

5. Temperatures from 175°C to room temperature are recommended for attapulgite synthesis, and temperatures below 140°C for sepiolite. At higher temperatures, the two minerals are unstable in the presence of aluminum ions.

6. In the lower temperature regions the reaction rate is slow and probably longer reaction times than used in this work will be needed.

7. Direct chemical analysis of the products is believed to be more accurate than the chemical analysis of the supernatant solution as employed in this investigation.

8. The different hypotheses of the origin of attapulgite and sepiolite should be examined in further detail.

APPENDICES

APPENDIX A

METHODS OF CHEMICAL ANALYSIS

Methods for determining soluble silica and aluminum and the solution technique for the analysis of silicates are presented in this section.

Determination of Silica in Solution[54]

Procedure. A suitable aliquot of sample solution is added to a 50-ml volumetric flask, acidified with 10 ml 1 N H_2SO_4 and followed by 10 ml of 0.3 M (with respect to MoO_4^{-2}) ammonium molybdate. The latter solution is prepared by dissolving 52.97 g of crystalline $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ in one litre of water with sufficient sodium hydroxide to give a pH of not less than 7.0. The sample is diluted to 50 ml with distilled water. The absorbance is measured at 400 mμ (at a slit width of 0.04 mμ when using a Beckman Model DU spectrophotometer). The reaction with monosilicic acid is complete within 2 min and if the proportion of monosilicic acid is to be determined in an aqueous sample, the reading should be taken at 2 min; if total silica is being determined (which, of course, will be present as monosilicic acid after sample treatment) the reading should be taken not sooner than 2 min nor later than 10 min after addition of ammonium molybdate.

Calculation of the silica content is made by reference to a standard curve. Standard silica solutions may be prepared either directly by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9\ H_2O$) in distilled water acidified with H_2SO_4 so that the final pH is about 1.5 (about 60 ml 1 N H_2SO_4 per litre) or by fusion of standard felspar or pure quartz in the same manner as outlined for preparing solid samples for silica determinations. The concentration of the stock solution should not be greater than 100 ppm SiO_2; 50 ppm SiO_2 was found to be suitable. Aliquots of the standard solution are used to prepare a standard curve for concentrations up to about 2 mg SiO_2 per 50 ml. It is important that the standard determinations should be made with the same reagents present in the same amounts as the unknown samples.

Determination of Aluminum in Solution[55]

8-Hydroxyquinoline Method

Aluminum can be completely extracted by 0.1 M HO_x in chloroform in the pH range 4.5-11. This extraction is not selective but many interfering metals can be removed by a preliminary extraction by 8-hydroxyquinaldine (HMO_x).

Procedure. To 10 ml of the solution containing not more than 200 μg of aluminum add 0.5 M sodium acetate to bring the pH to 4.0. This solution is then equilibrated for 15 minutes with two portions of a 1 percent solution of HMO_x in chloroform. Add to the aqueous phase 1 ml of 0.2 M sodium potassium tartrate (to prevent the precipitation of aluminum hydroxide) and an ammonia-ammonium chloride buffer to bring the solution to pH 10. Extract the solution again with two successive portions of 1 percent HMO_x

in chloroform (10 minutes shaking) and then remove remaining traces of the reagent by extraction with 5 ml of chloroform. Aluminum that remains in the aqueous phase is then extracted for 5 minutes with 10 ml of 0.10 M HO_x in chloroform and the absorbancy of aluminum oxinate is measured at 390 mμ.

Only uranium (VI) and zirconium (IV) interfere. Uranium (VI) can be masked at pH 9.5-10 by a saturated solution of ammonium carbonate, and zirconium can be removed by a preliminary extraction with cupferron from 1 N sulfuric acid.

Solution Technique for Analysis of Silicates[56]

Experimental

Preparation of Sample Solution. Reagents Required. Lithium metaborate, anhydrous, $LiBO_2$. The reagent should be examined spectrographically for impurities.

Lithium metaborate may be purified as follows: Dissolve 100 grams of $LiBO_2$ in 1 liter of hot water. Filter while hot, and allow the filtrate to cool. Filter the precipitated octahydrate on a glass frit, and heat at 50° C. for 24 hours or more in a ventilated oven to produce the dihydrate. Transfer the dihydrate to a platinum dish and bring slowly up to 400° C. The dehydration is accompanied by a large volume increase, so that a capacious dish is necessary. Crush the product gently in an agate mortar and mix well before using.

Alternatively, equivalent amounts of reagent grade lithium carbonate and boric acid (both obtainable in powder form) may be thoroughly mixed and heated slowly. At about 180° and 200° C. reaction occurs, resulting in an increase in volume. Further heating to 400° C. yields a product which is essentially anhydrous $LiBO_2$. It is desirable to put the mixed reagent in a cold furnace and bring up to temperature over a period of some hours; otherwise boric acid may be lost, and the final product will contain too much alkali.

Cobalt Nitrate Stock Solution. Dissolve 113 grams of $Co(NO_3)_2 \cdot 6\ H_2O$ in 1 liter of water. Filter, and store in a tightly sealed bottle. Preparation of this concentrated solution avoids frequent restandardization.

Dilute Cobalt Nitrate. Dilute 50.00 ml of cobalt nitrate stock solution to exactly 1 liter with water.

Dissolving Solution (with cobalt internal standard). Dilute 50.00 ml. of dilute cobalt nitrate with 30 ml. of concentrated

nitric acid to exactly 1 liter with water.

Solution Preparation. Mix 0.1000 gram of -200-mesh sample with 0.500 gram of lithium metaborate, transfer to a pre-ignited high-purity graphite crucible, and place in a muffle furnace at 950° C. for 10 to 15 minutes. Using a transfer pipet, put 50.0 ml. of dissolving solution in a flat-bottomed 200-ml. Teflon or polypropylene beaker. Add a Teflon-covered stirring bar. Remove the crucible from the furnace, swirl to gather uncoalesced beads of molten material, and pour the melt into the beaker. Cover the limit evaporation loss, and stir gently over a magnetic stirring unit (without heating) until solution is complete. Transfer the solution to a clean glass bottle with a tightly fitted plastic stopper (Kimble 60975-L).

Loss by spattering, either during fusion or in the addition of the molten material to the dilute acid, does not occur. The fusion does not wet the graphite, and none of the sample remains in the crucible if the operation is properly performed. Crucibles may be used many times without contamination.

Flux and sample must be well mixed before fusion; otherwise, local concentrations of silica in the melt may lead to slow or incomplete solution. Glass beakers should not be used.

Solutions of a few samples high in silica--e.g., glass sand--are apt to show a small residue of undissolved polysilicic acid; otherwise almost all rocks are easily dissolved. Care is necessary to prevent sodium contamination. Other sample weights and solution volumes may be used, but the recommended proportions of sample, flux, and nitric acid are nearly optimum, and should be approximately maintained.

APPENDIX B

DATA FOR THE Mg-Al-SiO_2 REACTION AT ROOM TEMPERATURE

This section presents the reaction data of the various tests at room temperature. Initial composition of the solution, initial and final pH, composition of residue product, and the result of its identification by x-ray diffraction are listed. The composition of the residue product is calculated by determining the final composition of the mother solution. For example, calculation for the composition of the residue product from Test No. 3 is presented below.

Solution	Composition		
	ppm Mg	ppm Al	ppm SiO_2
Initial	9.9	10.9	76.8
Final	0.06	2.6	50.0
Difference	9.84	8.3	26.8

	Composition of Residue	
		Weight %
$MgO = 9.84 \times 1.66 =$	16.32	27.8
$Al_2O_3 = 8.3 \times 1.89 =$	15.70	26.7
$SiO_2 =$	26.80	45.5
	58.82	100.0

Table 10. Reaction Data at 25°C of Mg-Al-SiO_2 in Solution

Test No.	Initial Solution (ppm)			pH		Reaction Product (Weight Percent)			X-ray Identification
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	
1	9.9	10.9	76.8	7.0	7.5	0	22.6	77.4	poorly crystal.
51	"	"	"	8.0	7.7	31.7	46.5	21.8	" "
2	"	"	"	9.0	7.9	0	10.3	89.7	" "
52	"	"	"	10.0	8.9	39.9	40.8	19.3	" "
3	"	"	"	11.0	10.4	27.8	26.7	45.5	" "
4	9.9	32.7	57.6	7.0	6.8	0	66.5	33.5	montmorillonoid
53	"	"	"	8.0	7.8	1.2	57.1	41.7	"
5	"	"	"	9.0	8.0	2.6	46.4	51	"
54	"	"	"	10.0	8.4	6.7	49.6	43.7	poorly crystal.
6	"	"	"	11.0	10.5	21.9	36	43.1	" "
7	29.7	10.9	57.6	7.0	7.5	0	47.4	52.6	poorly crystal.
55	"	"	"	8.0	7.7	0	48.6	51.4	" "
8	"	"	"	9.0	7.9	0	34.3	65.7	" "
56	"	"	"	10.0	8.2	15.8	29.8	54.4	" "
9	"	"	"	11.0	9.7	44.8	18.3	36.9	" "

Table 10. (Continued)

Test No.	Initial Solution (ppm)			pH		Reaction Product (Weight Percent)			X-ray Identification
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	
10	29.7	21.8	48	7.0	6.8	0	62.4	37.6	montmorillonoid
57	"	"	"	8.0	7.7	3.5	52.9	43.6	poorly crystal.
11	"	"	"	9.0	7.9	2.8	49.4	47.8	" "
58	"	"	"	10.0	8.1	15.8	40.5	43.7	" "
12	"	"	"	11.0	10.2	41	29	30	" "
13	19.8	32.7	48	7.0	6.7	0	67.4	32.6	montmorillonoid
59	"	"	"	8.0	7.8	2.7	59.6	37.7	"
14	"	"	"	9.0	8.0	1.0	58.3	40.7	"
60	"	"	"	10.0	8.5	11.3	48.6	40.1	poorly crystal.
15	"	"	"	11.0	10.0	29.6	34.4	36	" "
16	49.5	10.9	38.4	7.0	7.3	0	53	47	poorly crystal.
61	"	"	"	8.0	7.5	0	50.2	49.8	" "
17	"	"	"	9.0	7.7	0	43.9	56.1	" "
62	"	"	"	10.0	8.0	29	29.1	41.9	" "
18	"	"	"	11.0	9.9	58.6	15.5	25.9	" "

Table 10. (Continued)

Test No.	Initial Solution (ppm)			pH		Reaction Product			
						Weight Percent			X-ray
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	Identification
28	64.3	10.9	24	7.0	7.3	0	60.4	39.6	poorly crystal.
69	"	"	"	8.0	7.5	10	49.8	40.2	" "
29	"	"	"	9.0	7.9	26.5	38	35.5	" "
70	"	"	"	10.0	8.4	51.0	24.6	24.6	" "
30	"	"	"	11.0	9.9	69.4	15.3	15.3	double hydroxide
31	24.7	54.5	24	7.0	6.7	0	77.1	22.9	gibbsite
71	"	"	"	8.0	7.8	0	82.9	17.1	"
32	"	"	"	9.0	8.3	2.3	81.7	16	"
72	"	"	"	10.0	9.0	17.4	67.6	15	" + mont.
33	"	"	"	11.0	10.1	37	42.1	20.9	" + double hydroxides
34	54.4	32.7	14.4	7.0	6.7	0	80.6	19.4	gibbsite
73	"	"	"	8.0	7.8	0	85.4	14.6	"
35	"	"	"	9.0	8.2	12.1	73.9	14	"
74	"	"	"	10.0	8.5	46.8	44	9.2	" + double hydroxides
36	"	"	"	11.0	9.7	53.7	39.2	7.1	gibbsite + dble. hydroxides

Table 10. (Continued)

Test No.	Initial Solution (ppm)			pH		Reaction Product			
						Weight Percent			X-ray
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	Identification
37	19.8	76.3	9.6	7.0	6.8	0	87.5	12.5	gibbsite
75	"	"	"	8.0	7.7	0.6	94.1	5.3	"
38	"	"	"	9.0	8.5	3.4	92.6	4	"
76	"	"	"	10.0	9.5	16.7	78.4	4.9	"
39	"	"	"	11.0	10.1	21.6	72.6	5.8	" + brucite + dble. hydrox.
40	44.5	49.1	9.6	7.0	6.8	0	88.5	11.5	gibbsite
77	"	"	"	8.0	7.6	1.8	90.8	7.4	"
41	"	"	"	9.0	8.5	13.3	80	6.7	"
78	"	"	"	10.0	8.6	33.8	60.6	5.6	" + double hydroxides
42	"	"	"	11.0	10.3	53.6	40.1	6.3	gibbsite + dble. hydroxides + brucite
43	69.3	21.8	9.6	7.0	7.1	0	85	15	gibbsite
79	"	"	"	8.0	7.9	2.6	82.2	15.2	"
44	"	"	"	9.0	8.2	32.2	56.3	11.5	" + double hydroxides
80	"	"	"	10.0	8.5	60.6	33.3	6.1	gibbsite + "
45	"	"	"	11.0	10.2	69	25.5	5.5	" "

Table 10. (Continued)

Test No.	Initial Solution (ppm)			pH		Reaction Product			
						Weight Percent			X-ray
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	Identification
46	79.2	10.9	9.6	7.0	7.1	0	78.6	21.4	poorly crystal.
81	"	"	"	8.0	7.7	16.9	61.8	21.3	" "
47	"	"	"	9.0	8.0	43.4	40.6	14	double hydroxide
82	"	"	"	10.0	8.5	63.2	26.9	9.9	" "
48	"	"	"	11.0	10.2	76.5	16.3	7.2	" "
83	99	109	82	7.0	6.6	0	66.6	33.4	montmorillonoid
84	"	"	"	8.0	8.5	2.9	70.5	26.6	gibbsite + mont.
85	"	"	"	9.0	8.7	15.7	61.2	23.1	" + "
86	"	"	"	10.0	8.8	22	56.4	21.6	" + double hydrox. + mont.
87	"	"	"	11.0	9.9	34.2	47.8	18	double hydroxide + mont.
88*	99	109	82	7.0	7.15	0	74.9	25.1	montmorillonoid
89*	"	"	"	8.0		2.7	70.5	26.8	gibbsite
90*	"	"	"	9.0		16.2	60.9	22.9	poorly crystal.
91*	"	"	"	10.0	8.9	20.3	57.4	22.3	dbl. hydro. + mont.
92*	"	"	"	11.0	9.9	33.5	48	18.5	dbl. hydro.

*Tests No. 88-92 also contain 22 ppm Fe^{3+}.

Table 10. (Concluded)

Test No.	Initial Solution (ppm)			pH		Reaction Product			
						Weight Percent			X-ray
	Mg	Al	SiO_2	Initial	Final	MgO	Al_2O_3	SiO_2	Identification
93	49.5	21.8	78.1	11.0	9.5	44.5	21.4	34.1	poorly crystal.
94	"	"	42.2	11.0	10.0	52.7	25.9	21.4	double hydroxide
95	"	"	25.3	11.0	9.9	57.7	28.7	13.6	" "
96	"	43.6	76.8	11.0	9.7	37.7	32	30.3	poorly crystal.
97	49.5	10.9	26.4	11.0	10.0	64	16.3	19.7	dbl. hydroxide + mont.
98	"	43.6	"	11.0	9.7	44.1	42.8	13.1	" "
99	"	"	42	11.0	9.3	40	39.9	20.1	" "
103*	49.5	21.8	27	7.0	6.9	0	71.7	28.3	montmorillonoid
104*	"	"	"	8.1	7.6	8.4	59.7	31.9	poorly crystal.
105*	"	"	"	9.0	7.8	11.1	57.5	31.4	" "
106*	"	"	"	10.0	7.9	34.8	40.3	24.9	" "
107*	"	"	"	11.0	9.8	58.2	29.3	12.5	double hydroxide

*Tests No. 103-107 also contain 10 ppm Ca^{2+}.

APPENDIX C

ACID-DISSOLUTION DATA OF ATTAPULGITE AND SEPIOLITE

The reaction data of attapulgite and sepiolite with different acid concentrations and at various temperatures are listed here. In most cases, the soluble Mg, Al, and Fe were analyzed. The amount of each of the residual ions was calculated by subtracting the percent soluble from the total percent in the sample. For high percent soluble ions, the amount of residual Mg, Al, and Fe was determined directly from the insoluble residue.

Table 11. Attapulgite Reaction with 5.0 N HCl at 60° C

Reaction Time hours	Percent MgO Unreacted	Percent Al_2O_3 Unreacted	Percent Fe_2O_3 Unreacted
0	12.41	7.98	2.505
2.0	7.13	5.67	1.505
4.0	6.03	5.14	1.354
8.0	4.71	4.36	1.074
12.0	3.66	3.615	0.851
18.0	2.29	2.70	0.532

Table 12. Attapulgite Reaction with 5.0 N HCl at 70.3° C

Reaction Time hours	Percent MgO Unreacted	Percent Al_2O_3 Unreacted	Percent Fe_2O_3 Unreacted
0	12.41	7.98	2.505
1.0	8.0	5.68	1.605
2.0	7.09	5.14	1.413
4.0	4.4	4.23	1.0
6.0	3.105	3.575	0.788
8.0	2.075	2.785	0.539
10.0	1.494	2.305	0.402

Table 13. Attapulgite Reaction with 5.0 N HCl at 80.1°C

Reaction Time hours	Percent MgO Unreacted	Percent Al_2O_3 Unreacted	Percent Fe_2O_3 Unreacted
0	12.41	7.98	2.505
0.5	7.15	5.57	1.513
1.0	5.41	5.00	1.258
2.0	3.90	4.18	0.949
3.0	2.93	3.37	0.664
4.0	2.21	2.69	0.462

Table 14. Attapulgite Reaction with 4.0 N HCl at 91.2° C

Reaction Time hours	Percent MgO Unreacted	Percent Al_2O_3 Unreacted	Percent Fe_2O_3 Unreacted
0	12.41	7.98	2.505
0.5	5.16	5.08	1.213
1.0	3.52	3.82	0.848
1.5	2.34	3.01	0.566
2.0	1.535	2.40	0.399
2.5	0.919	1.752	0.265

Table 15. Attapulgite Reaction with 2.5 N HCl at 70.3° C

Reaction Time hours	Percent MgO Unreacted	Percent Al_2O_3 Unreacted	Percent Fe_2O_3 Unreacted
0	12.41	7.98	2.505
1.0	8.44	6.07	1.752
2.0	7.59	5.55	1.59
4.0	6.50	5.03	1.39
6.0	5.33	4.35	1.182
8.0	4.76	4.19	1.074
10.0	2.99	3.36	0.856

Table 16. Sepiolite Reaction with 1.0 N HCl at 30.5° C

Reaction Time hours	Percent MgO Unreacted
0	25.35
1.0	14.30
2.0	8.75
3.0	5.43
4.0	3.09

BIBLIOGRAPHY*

1. Yang, J. C. S., "The System Magnesia-Silica-Water Below 300°C," J. Am. Ceram. Soc., 43, 542-549 (1960).

2. Siffert, B., "Quelques Reactions de la Silice en Solution. La Formation des Argiles," Mem. Serv. Carte Geol. Als. Lor., No. 21.

3. Siffert, B. and R. Wey, "Synthese d'une Sepiolite a Temperature Ordinaire," Compt. Rend., 254, 1460-1462 (1962).

4. Preisinger, A., "Sepiolite and Related Compounds: Its Stability and Application," Clays and Clay Min., 10, 4-22 (1963).

5. Caillere, S., S. Henin, and J. Esteoule, "Nouvelles Etudes Sur la Synthese des Mineraux Argileux a Partir der Gels," Clay Min. Bul., 5, 272-278 (1962-64).

6. Bradley, W. G., "The Structural Scheme of Attapulgite," Am. Mineral., 25, 405-410 (1940).

7. Nagy, B. and W. F. Bradley, "The Structural Scheme of Sepiolite," Am. Mineral., 40, 885-892 (1955).

8. Brauner, K. and A. Preisinger, "Structure of Sepiolite," Mineral. Petrog. Mitt., 6, 120-140 (1956).

9. Kerr, P. F., "Attapulgus Clay," Am. Mineral., 22, 534-550 (1937).

10. Reynolds, W. R., The Lithostratigraphy and Clay Mineralogy of the Tampa-Hawthorn Sequence of Peninsular Florida, Master's Thesis, Florida State University, 1962.

11. Bonatti, E. and O. Joensuu, "Palygorskite from Atlantic Deep Sea Sediments," Am. Mineral., 53, 975-983 (1968).

12. Parry, W. T. and C. C. Reeves, Jr., "Sepiolite from Pluvial Mound Lake, Lynn and Terry Counties, Texas," Am. Mineral., 53, 984-993 (1968).

---

*For the complete titles of all journals referred to, see Chemical Abstracts, 50, 1 (1956).

BIBLIOGRAPHY (Continued)

13. Heystek, H. and E. R. Schmidt, "The Mineralogy of the Attapulgite-Montmorillonite Deposit in the Springbok Flats, Transvaal," Geol. Soc. S. Afric, Trans., 56, 99-119 (1953).

14. Loughnan, F., "Palygorskite at Redbank Plains, Queensland," Royal Soc. Queensland, 71, 43-50 (1960).

15. Rogers, L., A. Martin, and K. Norrish, "Palygorskite from Queensland," Min. Mag., 30, 534-540 (1954).

16. Longchambon, H., "Sur les Constituants Mineralogiques Essentials des Argiles, en Particulier des Terres a Foulon," Compt. Rend. Acad. Sci. Paris, 201, 483-486 (1935).

17. Longchambon, H., "Sur les Characteristique des Palygorskites," Compt. Rend. Acad. Sci. Paris, 204, 55-58 (1937).

18. Lapparent, J. de, "Les Milieux Generateurs de la Montmorillonite et de la Sepiolite," Compt. Rend. Acad. Sci. Paris, 203, 553-555 (1936).

19. McClellan, G. H., Petrology of Attapulgus Clay in North Florida and Southwest Georgia, Ph.D. Thesis, University of Illinois, 1964.

20. Noll, W., "Mineralbildung im System Al_2O_3-SiO_2-H_2O," Neues Jahrb. Mineral. Geol., Beil. Bd. A., 70, 65-115 (1935).

21. Noll, W., "Ueber die Bildungsbedingungen von Kaolin, Montmorillonit, Sericit, Pyrophyllit, und Analcim," Mineral. Petrog. Mitt., 48, 210-246 (1936).

22. Henin, S. and S. Caillere, "Vue d'ensemble sur la Probleme de la Synthese des Mineraux Phylliteux a Basse Temperatures," Coll. Int. CNRS (Paris) Genese et Synthese des Argiles, 31-42 (1961).

23. DeKimpe, C., M. C. Gastuche, and G. W. Brindley, "Ionic Coordination in Alumino-Silicic Gels in Relation to Clay Mineral Formation," Am. Mineral., 46, 1370-1381 (1961).

24. DeKimpe, C., M. C. Gastuche, and G. W. Brindley, "Low-temperature Systneses of Kaolin Minerals," Am. Mineral., 49, 1-16 (1964).

25. Caillere, S., J. Esteoule, and S. Henin, "Preparation de Silicates Alumino-Magnesiens a Partir de Gels," Compt. Rend. Acad. Sci. Paris, 254, 2380-2382 (1962).

BIBLIOGRAPHY (Continued)

26. Gastuche, M. C. and A. Herbillon, "Etude des Gels d'Alumine: Cristallisation en Milieu Desionise," Bull. Soc. Chem. Fr., 1404-1412 (1962).

27. Fripiat, J. J., A. Leonard, and N. Barake, "Relation Entre la Structure et la Texture des Gel de Silice," Bull. Soc. Chim. Fr., 122-140 (1963).

28. Iiyama, J. T. and R. Roy, "Controlled Synthesis of Heteropolytypic (Mixed-Layer) Clay Minerals," Clays and Clay Min., 10, 4-22 (1963).

29. Granquist, W. T. and S. S. Pollack, "Clay Mineral Synthesis," Am. Mineral., 52, 212-226 (1967).

30. Poncelet, G. M. and G. W. Brindley, "Experimental Formation of Kaolinite from Montmorillonite at Low Temperatures," Am. Mineral., 52, 1161-1173 (1967).

31. DeKimpe, C. R. and J. J. Fripiat, "Kaolinite Crystallization from H-Exchanged Zeolites," Am. Min., 53, 216-230 (1968).

32. Mumpton, F. A. and R. Roy, "New Data on Sepiolite and Attapulgite," Clays and Clay Minerals, 3, 136-143, (Oct. 8-10, 1956).

33. Esteoule, M. Jacques, "Synthese d'une Argile Fibreuse a Partir d'un Gel Alumino-Silicique a Basse Temperature," Compt. Rend. Acad. Sci. Paris, 260, 1686-1688 (1965).

34. Garrels, R. M. and F. T. Mackenzie, "Equilibrium Concepts of Natural Water Systems," Am. Chem. Soc., Adv. in Chem. Series, 67, 234-235 (1967).

35. Wollast, R., F. T. Mackenzie, and O. P. Bricker, "Experimental Precipitation and Genesis of Sepiolite at Earth-Surface Conditions," Am. Mineral., 53, 1645-1662 (1968).

36. Keller, W. D., William D. Balgord, and A. L. Reesman, "Dissolved Products of Artificially Pulverized Silicate Minerals and Rocks: Part I," Jour. Sed. Pet., 33, 191-204 (1963).

37. Reesman, A. L. and W. D. Keller, "Calculation of Apparent Standard Free Energies of Formation of Six Rock-forming Silicate Minearls from Solubility Data," Am. Mineral., 50, 1729-1739 (1965).

38. Reesman, A. L. and W. D. Keller, "Aqueous Solubility Studies of High-Alumina and Clay Minerals," Am. Mineral., 53, 929-942 (1968).

BIBLIOGRAPHY (Continued)

39. Kittrick, J. A., "Free Energy of Formation of Kaolinite from Solubility Measurements," Am. Mineral., 51, 1457-1466 (1966).

40. Hostetler, P. B. and C. L. Christ, "Studies in the System MgO-SiO_2-CO_2-H_2O (I): The activity-Product Constant of Chrysotile," Geochim. et Cosmochim. Acta, 32, 485-497 (1968).

41. Brindley, G. W. and R. F. Youell, "A Chemical Determination of Tetrahedral and Octahedral Aluminum Ions in a Silicate," Acta. Crist., 4, 495-496 (1951).

42. Osthaus, B. B., "Chemical Determination of Tetrahedral Ions in Nontronite and Montmorillonite," Clay and Clay Min., NAS 327, 404-417 (1954).

43. Osthaus, B., "Kinetic Studies on Montmorillonites and Nontronite by the Acid-Dissolution Technique," Clays and Clay Min., 3, 301-321 (1956).

44. Granquist, W. T. and G. Gardner Sumner, "Acid Dissolution of a Texas Bentonite," Clays and Clay Minerals, 6, 292-308 (1959).

45. Gastuche, M. C., "Kinetics of Acid Dissolution of Biotite," Int'l. Clay Conference, Stockholm I, 67-83 (1963).

46. Caillere, S. and S. Henin, "Occurrence of Sepiolite in the Lizard Serpentine," Nature, 163, 962 (1949).

47. Serdyuchenko, D. P., "Sepiolite from Northern Caucasus," Doklady Acad. Nauk U.S.S.R., 69, 577-580 (1949).

48. Stephen, I., "An Occurrence of Palygorskite in the Shetland Isles," Mineralog. Mag., 30, 471-480 (1954).

49. Demangeon, P. and H. Salvayre, "Sur la Genese de Palygorskite dans un Calcaire Dolomitique," Bull. Soc. Fr. Miner. Crist., LXXXIV, 201-202 (1961).

50. Shabayeva, Ye, A., "Palygorskite from the Paleogene Beds of Southern Turkmenia," Translated from Doklady Acad. Sci. U.S.S.R. by Am. Geol. Inst., 143, 94-97 (1962).

51. Millot, G., J. Lucas, and R. Wey, "Research on Evolution of Clay Minerals and Argillaceous and Siliceous Neoformation," Clays and Clay Min., 10, 399-412 (1963).

52. Buie, B. F. and L. R. Gremillion, "Attapulgite in Fuller's Earth Deposits of Georgia and Florida," Georgia Mineral Newsletter, XVI, 20-25 (1963).

BIBLIOGRAPHY (Concluded)

53. Gremillion, L. R., The Origin of Attapulgite in the Miocene Strata of Florida and Georgia, Ph.D. Thesis, Florida State University, 1965.

54. Govett, G. J. S., "Critical Factors in the Colorimetric Determination of Silica," Anal. Chim. Acta., 25, 79 (1961).

55. Riley, J. P. and H. P. Williams, "Determination of Aluminum in the Presence of Interfering Elements," Mikrochim. Acta., 8, 825-830 (1959).

56. Suhr, N. H. and C. O. Ingamells, "Solution Technique for Analysis of Silicates," Anal. Chem., 38, 731 (1966).

57. Feitkecht, W., "Über die Bildung von Doppelhydroxyden Zwischen Zwei und Dreiwertigen Metallen," Helvetica Chem. Acta., 25, 555-569 (1942).

58. Feitkecht, W. and M. Gerber, "Zur Kenntnis der Doppelhydroxyde und Basischen Doppelsalze III: Über Magnesium-Aluminiumdoppelhydroxyd," Helvetica Chem. Acta., 25, 131-137 (1942).

59. Mortland, M. M. and M. C. Gastuche, "Crystallization of Mixed Hydroxides of Magnesium and of Aluminum in a Dialysis Medium," Comptes Rendus, 255, 2131-2133 (1962), in French.

60. Klotz, I. M., Chemical Thermodynamics, Prentice-Hall, New Jersey, 1960, pp. 329-332.

61. Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," U.S. Nat. Bur. Stand. Circ. 500 (1952).

62. Levenspiel, O., "Chemical Reaction Engineering," John Wiley and Sons, Inc., New York, 1962, p. 435.

63. Walker, P. L., Jr., F. Rusinko, Jr., and L. G. Austin, "Gas Reactions of Carbon," Advances in Catalysis, XI, 133-221 (1959).

64. Mering, J., "Les Reactions de la Montmorillonite," Bull. Soc. Chim. Fr., D218-D223 (1949).

VITA

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